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DIVISION OF THE
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M. M. LEIGHTON, *Chief*
URBANA

REPORT OF INVESTIGATIONS—NO. 117

SOUTHERN ILLINOIS NOVACULITE AND NOVACULITE GRAVEL FOR MAKING SILICA REFRACTORIES

BY

C. W. PARMELEE AND C. G. HARMAN
DEPARTMENT OF CERAMIC ENGINEERING
UNIVERSITY OF ILLINOIS

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BY

C. W. Parmelee and C. G. Harman

Department of Ceramic Engineering
University of Illinois

ABSTRACT

Extensive deposits of massive chert known as novaculite and of novaculite gravel are found in Alexander and Union counties in southern Illinois. The novaculite is a cryptocrystalline material, mine-run samples of which contain approximately 97 percent silica; selected samples have a slightly higher silica content. The novaculite gravel contains a small amount of clay. Other highly siliceous materials found in the general area are ganister, a naturally granular material, and tripoli or silica, a material consisting mostly of minute particles.

The ganister has been used successfully in the manufacture of refractories, but efforts to use the novaculite for this purpose have encountered difficulties that have raised doubts as to its suitability. The object of this investigation was to determine whether or not the novaculite and the novaculite gravel have value for the manufacture of silica bricks and shapes for lining furnaces that are operated at high temperatures. The very large tonnages of silica refractories manufactured in Illinois from ganister shipped in from other states indicates the desirability of finding in Illinois a supply of an equally useful material.

Because of their importance in the manufacture and use of silica refractories, the following properties of novaculite and novaculite gravel and of silica refractories made from them were given particular attention: (1) Nature and rate of inversion; and (2) mechanical strength in relation to particle size, packing, and fluxes.

Both the novaculite and the novaculite gravel, which contained a small amount of clay, were separately crushed and screened to grade them according to size. Trial mixtures of different proportions of each size grade were made. The minimum amount of voids obtained in the crushed novaculite subjected to a packing pressure of 7000 pounds per square inch was 8.2 percent. Under similar conditions the novaculite gravel tests gave a minimum of 2.5 percent voids. Washed crushed novaculite mixed in the proportions: 35 percent coarse fraction, 15 percent medium fraction, and 50 percent fine fraction, when moistened with 4 percent water and packed under a pressure of 3000 pounds per square inch, gave a product having a porosity of 19 percent.

In the study of the influence of various amounts of several kinds of fluxes on the southern Illinois materials, calcium oxide, which is the flux usually employed in the manufacture of silica brick, was used as a standard of reference. Thirteen other oxides, compounds, and mixtures were tried as a flux and accelerator. Sodium tungstate proved to be the most vigorous accelerator and borax was a close second. Interesting results were observed with iron oxide, both alone and in a combination with other fluxes. The calcium oxide was somewhat less effective than these three.

The work on the effect of particle size of novaculite and novaculite gravel on inversion in the presence of lime showed that the finer sizes of the material reached a stable state of inversion more quickly than the coarser material, and that the coarse material showed greater swelling and cracking.

Cristobalite was the product of the inversion. A comparison of the inversion rates of the novaculite, tripoli, and ganister from Baraboo, Wisconsin (a quartzite largely

used in the manufacture of silica brick) proved the Illinois materials to be identical in conduct and to have much faster rates of inversion than the Baraboo quartzite and to have a significant development of tridymite at a lower temperature, which is a distinct advantage.

The foregoing data were applied to the preparation and forming of standard size 9-inch brick from the crushed sized novaculite. The results confirmed the earlier findings that the grain size determines the percentage of voids, hence the strength. The strength is also influenced by the amount and kind of bond and the manner of firing. Illinois novaculite—crushed, graded, and bonded with lime—gave a product correspondingly close in its character and properties to the commercial silica brick. These brick were fired in the kilns of the Department of Ceramic Engineering at the University of Illinois and in a commercial kiln.

It was further found that better brick can be made by mixing with the Illinois novaculite a certain proportion of the extremely fine-grained silica or tripoli obtainable in the same area of southern Illinois as the novaculite and novaculite gravel.

In summary, the results of this investigation indicate that Illinois novaculite, when crushed, properly graded, bonded, and fired furnishes a silica refractory similar in appearance and properties to the commercial silica brick made from quartzite ganister.

PART I—PROPERTIES OF NOVACULITE AND NOVACULITE GRAVEL

Introduction

RESOURCES AND SAMPLES

A variety of high-silica materials, among them novaculite, novaculite gravel, ganister, and tripoli, also known as "amorphous" silica, are found in Alexander and Union counties of extreme southern Illinois. Although the gravel is used in some quantity as road metal, the other materials find only limited commercial use. The first two materials are chert, the term novaculite being commonly applied in southern Illinois to deposits that consist of solid layers of chert, and the term novaculite gravel to a gravel that consists of angular chert fragments with which is associated usually a small amount of red or yellow clay and varying amounts of tripoli. The ganister of southern Illinois is a highly siliceous material which has naturally a loose texture somewhat similar to that of cornmeal. The tripoli or silica consists principally of a microcrystalline form of silica so small that the material has been referred to as amorphous or cryptocrystalline. The natural deposits have varying degrees of coherency and the material is ground and sized for use.

There are large deposits of each of these materials, although the size and number of ganister deposits is believed to be less than that of novaculite and novaculite gravel. The novaculite gravel deposits are known to be as much as 120 feet thick, the novaculite deposits are known to be at least 50 feet thick, and the ganister deposits have been worked ordinarily to a thickness of 10 to 15 feet but the total thickness may be considerably greater. The ganister ordinarily is mined underground whereas the novaculite and novaculite gravel are obtained from open pits.[1]

The samples used in this study were all obtained from fresh exposures in deposits which were being operated or had been operated recently. Because of the amount of work involved in testing, only a limited number of samples could be included in this investigation. The samples examined do not represent necessarily all the variations existing in the novaculite, novaculite gravel, and ganister deposits in southern Illinois. However, it is believed that the results of the tests do provide a basic picture of the nature and possible use of these materials in the making of silica brick, and that from the data the effects of variations in the character of the materials can be evaluated.

The samples studied were as follows:

Novaculite—from a 7-foot exposure of white novaculite with a few scattered light yellow spots, in the NE. $\frac{1}{4}$ NW. $\frac{1}{4}$ sec. 36, T. 14 S., R. 1 W., near Tamms, Illinois.

Novaculite gravel—pit-run gravel from a 120-foot exposure of reddish gravel in the NE. $\frac{1}{4}$ NW. $\frac{1}{4}$ sec. 36, T. 14 S., R. 1 W., near Tamms, Illinois.

Washed novaculite gravel—same as sample above but washed in the laboratory to remove clay and particles finer than 28 mesh.

Illinois ganister—mine-run material from a 12-foot exposure in a mine at the W. $\frac{1}{2}$ NW. $\frac{1}{4}$ NE. $\frac{1}{4}$ sec. 18, T. 14 S., R. 1 W., near Elco, Illinois.

Ganister—standard commercial material already ground, from Baraboo, Wisconsin. Used for purposes of comparison.

Quartzitic sandstone—pit-run material from a 40-foot exposure in a pit in the SW. $\frac{1}{4}$ sec. 12, T. 14 S., R. 6 E., near Tansil, Illinois.

Tripoli—a commercial product of the Illinois Mineral Company at Elco, Illinois.

PREVIOUS WORK ON SILICA REFRACTORIES

Many reports on silica and its use in manufacturing refractories have been published. The earliest extensive study of the temporary and permanent volume changes which silica undergoes upon heating (see fig. 1)

[1] For a discussion of the distribution and character of the cherty formations of Alexander and Union counties, see Illinois Geol. Survey Rept. Inv. No. 70.

was made by Fenner.[2] The significance to the industry of the fundamental research by LeChatelier, Sosman, McDowell, and others appears in any serious discussion of the material and its uses at high temperatures. The manner of the changes has been disclosed but the rates of change are not so well known, although we recognize that they are dependent upon the specific raw material used, its grain size, and the nature and the amount of impurities or additions of chemical agents used.

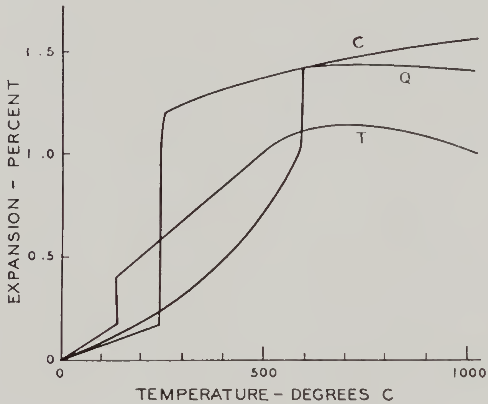

Fig. 1.—Low temperature inversions of silica: C, cristobalite; T, tridymite; Q, quartz.

RAW MATERIALS FOR SILICA REFRACTORIES

In the choice of raw materials for silica refractories, the main points considered are chemical purity, size of grain obtainable, and the magnitude of increase in volume upon heating.

For the manufacture of silica brick, the natural rock should contain at least 97 percent of silica and should not yield too fine a powder upon crushing. According to many writers, the order of merit of the natural forms of silica is given as chalcedony, old quartzites, and vein quartz. Quartz schists, sandstone, and sand are considered unsuitable, the first two on account of their structure and the presence of many impurities in the form of inclusions, and the latter two on account of their variability in composition and their excessive fineness after grinding.

The Illinois novaculite, which was the material under investigation, is a type of rock composed of a form of silica sometimes described as chalcedony. It has a cryptocrystalline structure and the individual crystals have mean diameters of 0.05 to 0.10 microns.[3] It is possible that a small amount of opaline is present. Minute quartz crystals are admixed with the chalcedony. It is well known to technologists familiar with the silica minerals that the cryptocrystalline variety, when heated at high temperature, is readily transformed, that is inverted, into the more useful cristobalite or tridymite. The Findling's "quartzite" of continental Europe, which has been a very important raw material for the silica brick industry of that area, is a cryptocrystalline silica. Ross[4] found that chert from Indiana, when strongly heated, showed density changes due to inversion which were regarded by him as favorable indications of the value of the material for silica brick.

Program of Work

The objective of this investigation was to discover whether Illinois novaculite could be used satisfactorily for the manufacture of silica brick and similar refractories. As the chemical and petrographic characteristics indicated that it should be suitable, and possibly superior to the siliceous rock ordinarily employed, it was necessary to study certain physical properties such as the crushing characteristics, the packing of the crushed rock, and the rates and completeness of the inversions which accompanied the use of several bonding agents or fluxes.

The crushing characteristics are important because they influence the mechanical strength and porosity of the finished brick or other forms. Silica refractories are unlike the clay refractories in several particulars. Clay undergoes progressive vitrification and therefore the porosity decreases with increased firing temperature, but silica brick does not show such a change until it has reached and passed its maximum safe-firing

[2] Fenner, C. N., Stability relations of the silica minerals: Am. Jour. Sci., vol. 36, p. 339, 1913.

[3] The micron is 10^{-4} millimeter or 0.000,001 m.

[4] Ross, Donald W., Silica refractories: U. S. Bur. Standards Tech. Paper No. 116, 1919.

temperature, then it collapses rather quickly. The maximum mechanical strength and minimum porosity of a refractory depend largely upon the relative proportions of the several sizes and shapes of the crushed rock used.

The crushed rock was screened into "coarse", "medium", and "fine" fractions, and experiments were made to determine what proportions of the various sizes or fractions should be used to obtain a mixture that would yield brick having the maximum mechanical strength and minimum porosity. The "packing" experiments are described in detail on pages 13-20.

The bonding agent also referred to as flux, is more important for its reaction in promoting the inversion of the chert to the most useful type of crystalline silica rather than for its actual bonding effect, and the amount is strictly limited to the minimum percentage required, usually two or three percent. Larger amounts react to diminish the refractoriness of the product. Clay, which is a most useful bonding material, cannot be used for this reason. The few agents which are practicable as accelerators are chosen because of their low cost and efficiency.

The research having defined the conditions of crushing to yield the desired grain sizes, the most suitable proportions of these sizes to furnish the minimum voids when the grains were packed together, the mechanical strengths of such mixtures, and the effects of various bonds or accelerators, the final phase of the work consisted of making samples of standard 9-inch brick, firing them, and comparing their physical properties with those of commercial silica brick.

ACKNOWLEDGMENTS

The investigation was done under the supervision of Professor Cullen W. Parmelee of the Department of Ceramic Engineering of the University of Illinois, with the assistance of Dr. Cameron G. Harman of the Survey staff.

Crushing Characteristics

SCREEN ANALYSIS OF NOVACULITE REDUCED IN LABORATORY SMOOTH ROLLS

The rock was reduced to 1¼ inches and finer in a jaw crusher and then put through small laboratory smooth rolls, adjusted as follows:

(g–2)—rolls about 1/8 inch apart.
(g–3)—rolls touching.
(g–4)—rolls about 3/32 inch apart.
(g–5)—rolls about 1/16 inch apart.
(g–6)—midway between g–4 and g–5.

The screen analysis of these grinds is shown in table 1.

Table 1.—Screen Analysis of Novaculite Reduced in Smooth Rolls

Sieve mesh[a]	Grind Number									
	g–2		g–3		g–4		g–5		g–6	
	%	Cum. %	%	Cum. %	%	Cum. %	%	Cum. %	%	Cum. %
Plus 8....	40.6	40.6	4.4	4.4	37.9	37.9	—	—	24.9	29.4
8 to 10..	8.0	48.6	2.5	6.9	9.7	47.6	4.5	4.5	13.0	42.4
10 to 14..	18.2	66.8	16.8	23.7	20.9	68.5	17.3	21.8	21.5	63.9
14 to 28..	13.6	80.4	33.1	56.8	14.4	82.9	36.7	58.5	16.1	80.0
28 to 48..	6.5	86.9	16.7	73.5	6.3	89.2	11.9	70.4	6.8	86.8
48 to 100.	3.0	89.9	8.9	82.4	3.3	92.5	10.4	80.8	3.6	90.4
100 to 200.	2.8	92.7	5.6	88.0	2.3	94.7	6.7	87.5	4.0	94.4
Minus 200.	9.3	100.0	12.0	100.0	5.2	99.9	12.6	100.1	6.0	100.4

[a]All screening analyses were made with Tyler Standard Screen Scale Sieves.

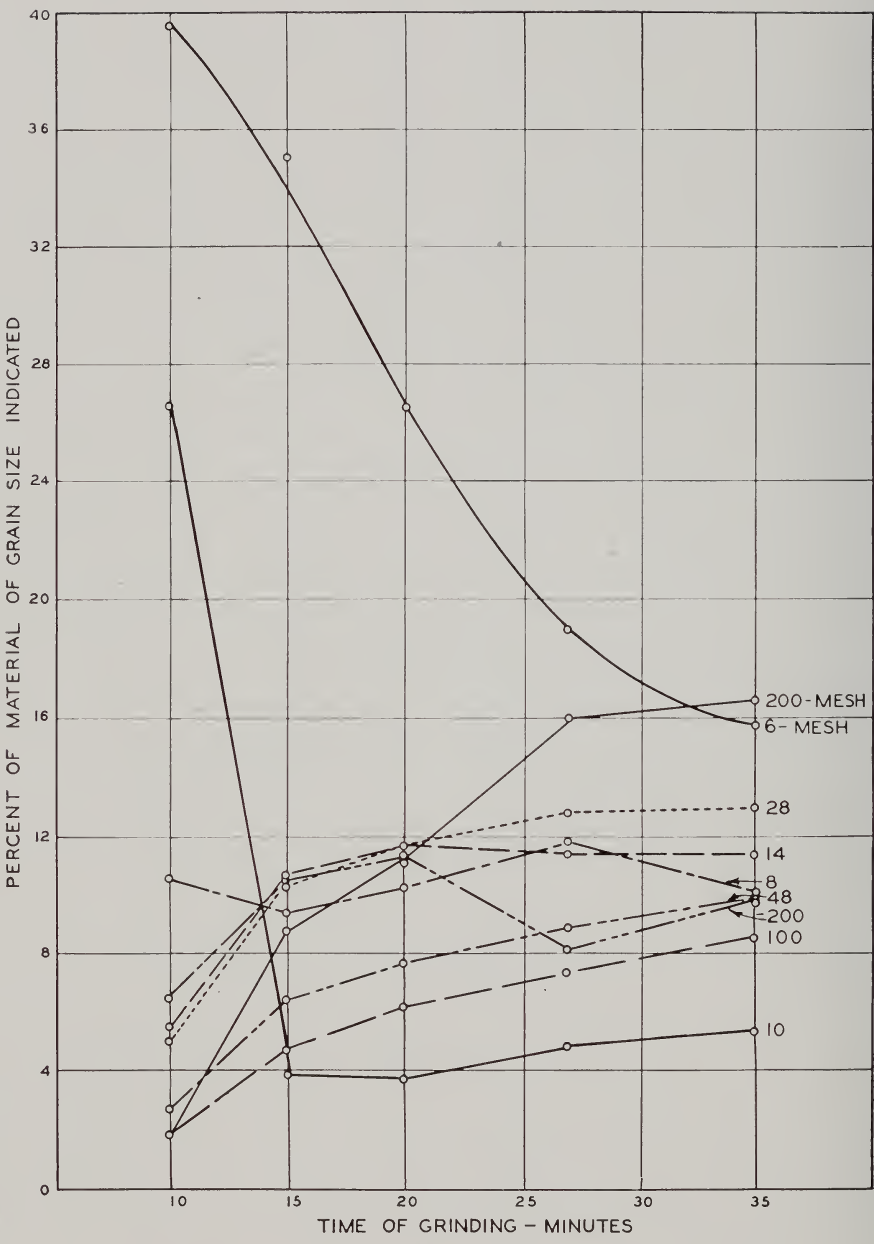

FIG. 2.—Rate of grinding of novaculite; 125-lb. charge in 5-foot wet pan. Curves represent percentage of material on the sieve indicated.

Table 2.—Screen Analysis of Mine-run Novaculite Gravel Ground Dry in a Wet Pan

Sieve mesh	Grinding Time									
	10 Min.		15 Min.		20 Min.		27 Min.		35 Min.	
	%	Cum. %	%	Cum. %	%	Cum. %	%	Cum. %	%	Cum. %
Plus 6....	39.6	39.6	35.1	35.1	26.5	26.5	19.0	19.0	15.7	15.7
6 to 8...	10.5	50.1	9.4	44.5	10.2	36.7	11.8	30.8	10.1	25.8
8 to 10..	26.6	76.7	3.9	48.7	3.7	40.4	4.3	35.6	5.3	31.1
10 to 14..	5.5	82.2	10.7	59.1	11.7	52.1	11.4	47.0	11.3	42.4
14 to 28..	5.0	87.2	10.3	69.4	11.7	68.3	12.8	59.8	12.9	55.3
28 to 48..	2.7	89.9	6.4	75.8	7.7	71.5	8.8	68.6	9.9	65.2
48 to 100.	1.8	91.7	4.7	80.5	6.2	77.7	7.3	75.9	8.5	73.7
100 to 200.	1.8	93.5	8.7	89.2	11.1	88.8	16.0	91.9	16.6	90.3
Minus 200.	6.5	100.0	10.5	99.7	11.3	100.1	8.1	100.0	9.8	100.1

SCREEN ANALYSIS OF NOVACULITE REDUCED IN A WET PAN

Novaculite was broken in a large jaw crusher, then 125-pound charges were put into a 5-foot wet pan and ground dry. Samples were taken for screen analysis at the end of 10 minutes, 15 minutes, 20 minutes, 27 minutes, and 35 minutes. The results of this test are shown in table 2 and figure 2.

EXPERIMENTS WITH PACKING CRUSHED NOVACULITE

The particle-size distribution has a very marked influence upon the physical properties of the brick. In general, the denser the packing, the stronger the final product. For maximum resistance to spalling, the balance between elasticity and mechanical strength must be correct, and these properties are both largely dependent upon the particle-size grading. It was therefore important to learn the manner in which the packed density varied with grain-size distribution.

Packing Characteristics of Three Grain-Size Mixtures

METHOD

A preliminary study of the packing characteristics of crushed novaculite was determined by a method similar to that used by Westman and Hugill.[5] Briefly it consisted of a capsule for holding a known weight of the sized grains whose volume could be calculated at any time during the test from the known internal dimensions of the container and the measured height of the sample therein. This capsule containing the sample was placed in an apparatus where it could be subjected to any desired number of impacts of a controlled magnitude. Measurements of the volume of the grains in the capsule were taken after each series of 500 impacts, and the minimum volume and closest packing were considered to be reached when there was no further reduction on repeated shaking.

RESULTS

The results of packing these fractions are shown in table 3 and figure 3 where the values plotted are the ratios of the bulk volumes to the true volumes. The lines on the diagram represent mixtures which pack with the same volume of voids. From the plotted data it may be seen that the sample containing 50 percent coarse fraction, 25 percent medium fraction and 25 percent fine fraction represents the densest packing mixture of this system.

In silica brick, particle-size distributions must be made which yield the most satisfactory balance of properties. This may be done only by trial. These grain-size studies were made in order to simplify practice for studies where control of grain size was necessary.

[5] Westman, A. E. R., and Hugill, H. R., The packing of particles: Jour. Am. Ceramic Soc., vol. 13, pp. 767–779, 1930.

TABLE 3.—PACKING OF DIFFERENT PRECENTAGES OF THREE GRAIN SIZES

Grain size—Screen mesh (percent)			Packed Vol. / True Vol.	Percent voids
Through 8 on 10	Through 28 on 48	Through 200		
50	..	50	1.43	37.5
25	..	75	1.49	32.8
75	..	25	1.40	28.2
..	25	75	1.54	35.2
..	75	25	1.52	33.3
..	50	50	1.42	29.5
75	25	..	1.62	38.2
..	50	50	1.60	37.5
..	25	75	1.63	38.9
100	..	..	1.77	43.7
..	100	..	1.77	43.8
..	..	100	1.63	38.8
70	15	15	1.44	30.5
50	25	25	1.29	22.5
40	30	30	1.34	25.6
60	20	20	1.39	27.9
50	20	30	1.32	24.3
50	15	35	1.33	24.8
50	30	20	1.33	24.7
45	30	25	1.31	23.9
45	25	30	1.30	23.1
55	20	25	1.33	24.8
55	25	20	1.34	25.7

PACKING OF MANY SIZES UNDER VARIOUS PRESSURES

Data obtained from packing of these sizes gives information for proportioning grains to yield well packed bodies, but in practice such "gap gradings" are not desirable. Instead "continuous" gradings are preferred. In addition the brick are formed by applying force, in some manner, to the mass being molded, which may influence the choice of grading. The packing of three sizes just described is useful by way of furnishing a starting point for a study of more detailed distributions.

To make these tests, samples of well mixed mine-run novaculite gravel and selected novaculite were placed in a mold and pressed. The mold was the same one used in preparing thermal expansion specimens, and is described below. (See fig. 8.) The volumes of the specimens were determined by measuring the height of the piston with a 1/1000 inch gage after application of pressure. The grain-size gradings studied are shown in table 4.

The percentage of voids in the samples after packing are tabulated in table 5. These samples were packed with 2½ cc. water per 25-gram sample.

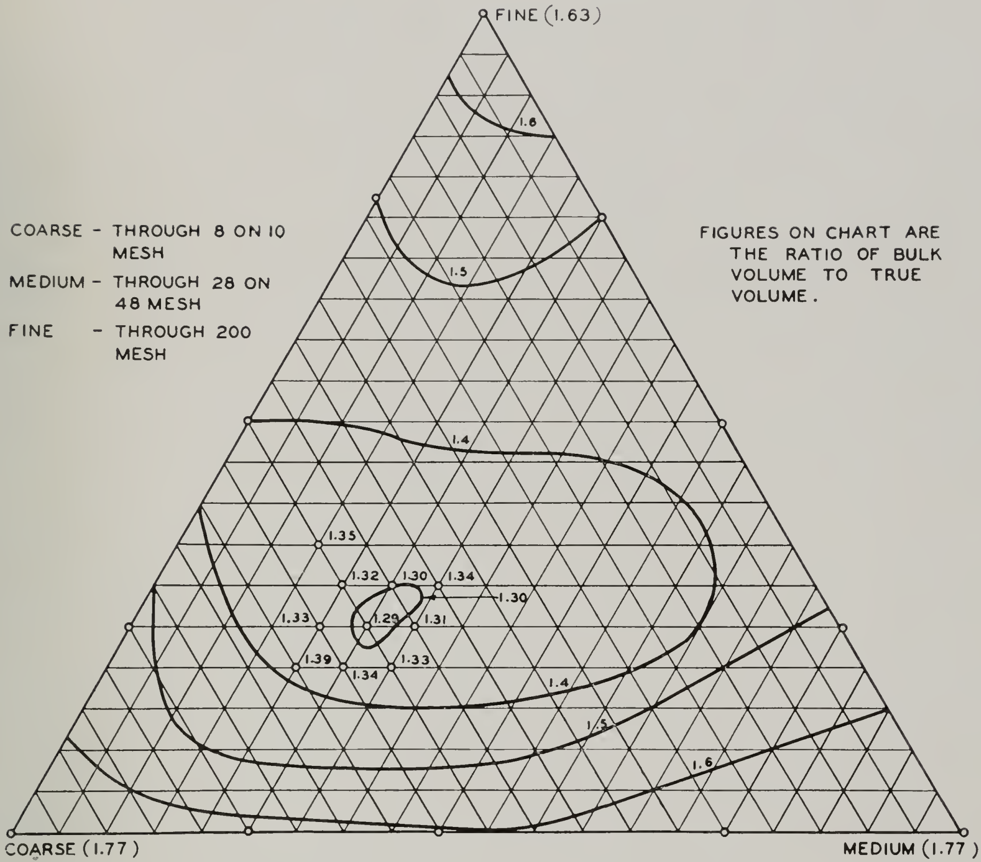

FIG. 3.—Packing of novaculite grains of three sizes.

P-1 is the mix that packed to maximum density in the three-sieve size mixture as shown in figure 3. Another test was made in which the novaculite finer than 200-mesh was replaced by an equal quantity of commercial tripoli. This tripoli is much finer in average grain size than the novaculite, averaging 200-mesh or finer in size. The results are given under P-2 in table 5. At 1000 pounds per square inch, P-1 packed to 28.4 percent voids, while at the same pressure, P-2 packed to 18.6 percent voids. At pressures of 2000 to 2500 pounds per square inch there was little difference in the degree to which these two mixtures packed. Further increase of pressure increased the density of P-2 at a greater rate than that of P-1.

Table 4.—Grain-size Distributions Used in Pressure Packing Tests
In weight percent

Made from Mine-run Novaculite Gravel

Screen mesh	Weight percent by mix number					
	P–3	P–4	P–5	P–6	P–7	P–9
6 to 8	23	23	15	7	..	27.6
8 to 10	7	7	7	7	7	....
10 to 14	7	7	7	7	7	10.6
14 to 20	6	6	6	6	6	11.8
20 to 28	7	7	7	7	7	9
28 to 48	13	13	13	13	13	10.5
48 to 100	13	13	13	13	13	5.5
100 to 200	14	14	14	14	14	3.5
Minus 200 (novaculite)	10	..	10	10	10	7.5
Minus 200 (tripoli)	..	10	8	16	23	15.0
	P–10	P–11	P–12	P–14	P–15	P–16
6 to 8	41.8	4.4	3.9	13.1	30.2	28.1
8 to 10	10.6	2.5	2.2	8.8	..	..
10 to 14	7.1	16.8	14.8	17.9	19.8	21.9
14 to 20	14.1	33.1	21.2	16.2	14.8	15.1
20 to 48	..	..	..	..	..	..
28 to 48	7.1	16.1	16.3	14.1	7.0	6.5
48 to 100	3.8	8.9	8.7	7.8–	3.3	3.4
100 to 200	2.3	5.6	5.5	5.4	3.1	2.3
Minus 200 (novaculite)	5.1	12.0	11.7	11.6	7.4	5.5
Minus 200 (tripoli)	17.4	..	7.8	5.3	14.4	17.2

Made from Selected Novaculite

Screen mesh	P–1	P–2	P–17	P–19	P–20	P–21
6 to 8	..	..	23	15	7	..
8 to 10	50	50	7	7	7	7
10 to 14	..	..	7	7	7	7
14 to 20	..	..	6	6	6	6
20 to 28	..	..	7	7	7	7
28 to 48	25	25	13	13	13	13
48 to 100	..	..	13	13	13	13
100 to 200	..	..	14	14	14	14
Minus 200 (novaculite)	25	..	10	10	10	10
Minus 200 (tripoli)	..	25	..	8	16	23

The mixtures shown in table 4 as P-9 to P-16 are of rocks crushed in the rolls as described above. P-11 (tables 4 and 5) is the same as g-3 in table 1. P-10 was produced from this by adding enough coarse to bring this fraction to about 50 percent and by adding sufficient tripoli to bring the fines to 25 percent. The result was a decided decrease in the volume of the voids. At 1000 pounds per square inch, P-11 had 24.8 percent voids, and at the same pressure the adjusted mix, P-10, had 16.0 percent voids. Other mixes, P-9 to P-16, showed the variations that might be expected from a variety of different grain-size mixtures.

Novaculite may be ground in a wet pan so that the cumulative percent of particles coarser than any screen is a linear function of the logarithm of the width of the screen opening (fig. 4). In order to test the

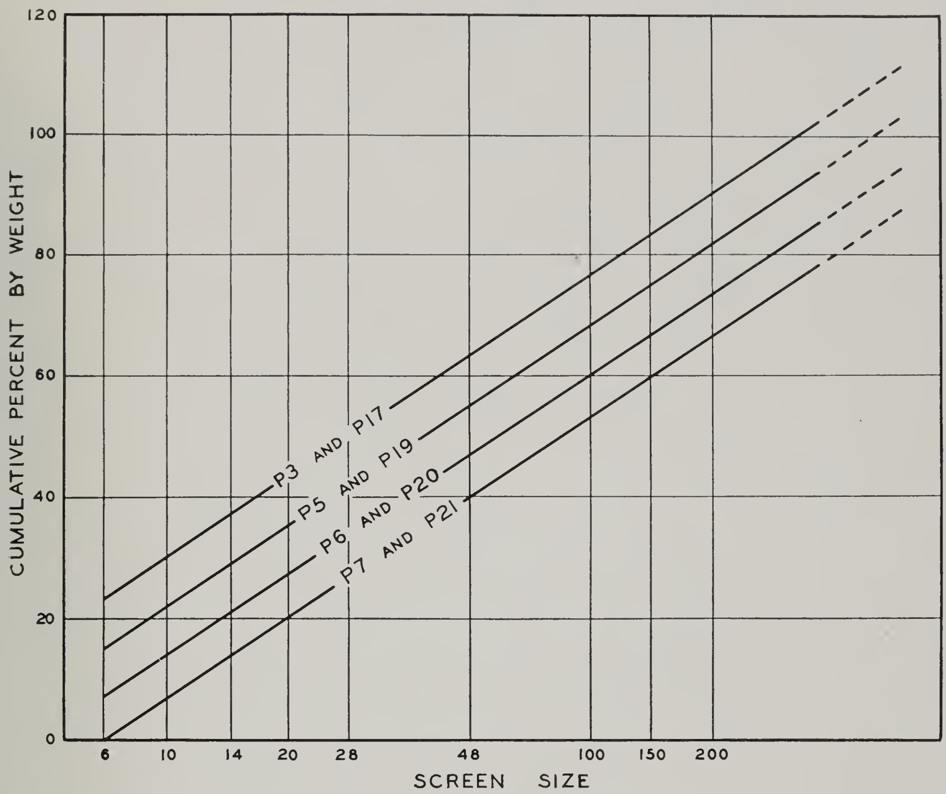

FIG. 4.—Graph illustrating the type of grain-size variation for packing experiments.

effect of the finest and coarsest fractions of grain sizes for this type of distribution, mixes P-3, P-4, P-5, P-6, and P-7 were made. The distribution of the sizes used are shown in table 4 and figure 4. These mixes were made from mine-run novaculite gravel which contains about 2 percent clay. P-3 may be considered as the base mix, in which the 6- to 8-mesh material was replaced by Illinois tripoli to produce P-5, P-6 and P-7. The results of packing this material are shown in table 5 and figure 5. These data showed that for this type of particle-size distribution, the conditions for minimum voids at pressures of less than 4000 pounds per square inch was about 19 percent through 200-mesh. This also implied about 14 percent 6- to 8-mesh material.

The series P-17, P-19, P-20, and P-21 were made of clear white novaculite which was free from clay. The purpose of this series was to determine the effect of clay upon the wet packing of grains. This series had the same screen analysis as the P-3 to P-7 series. The data on this series of mixes has been plotted in figure 6. A com-

TABLE 5.—RESULTS OF PRESSURE PACKING

Pressure on specimen lb. per sq. inch	Voids—Percent of bulk volumes																	
	Mix numbers																	
	P–3	P–4	P–5	P–6	P–7	P–9	P–10	P–11	P–12	P–14	P–15	P–16	P–17	P–19	P–20	P–21	P–1	P–2
1000	18.2	18.5	15.0	17.9	21.3	21.9	16.0	24.8	24.3	20.0	18.9	15.9	29.5	25.2	23.0	23.6	28.4	18.6
1500	16.3	17.8	12.1	15.6	19.2	....	....	....	21.6	17.7	15.7	14.1	26.9	22.7	20.1	21.0	17.0	15.9
2000	14.3	15.9	10.8	13.8	17.4	17.1	14.2	18.2	19.2	14.7	13.2	12.7	24.2	20.0	17.8	18.5	13.2	13.8
2500	12.4	14.0	8.6	12.3	15.8	15.6	12.4	16.2	17.2	12.9	11.6	11.2	23.0	18.4	16.2	17.5	12.7	13.1
3000	11.2	12.4	7.9	11.0	14.7	14.3	11.0	14.5	15.2	10.8	10.4	9.9	21.1	16.6	14.8	16.3	11.6	10.6
3500	9.7	11.2	6.9	10.0	13.4	13.1	9.6	12.9	14.2	9.3	....	8.9	19.5	15.4	13.5	15.1	10.5	9.3
4000	8.4	9.5	5.9	8.9	12.4	12.8	8.5	11.6	12.9	8.4	7.9	7.8	17.7	14.4	12.4	13.9	9.5	8.3
5000	5.9	8.4	4.7	7.6	11.1	11.6	7.2	9.2	11.0	6.4	6.6	6.1	16.3	13.0	11.2	13.0	9.0	7.3
6000	4.9	7.3	3.9	6.6	10.3	10.0	6.0	6.4	9.8	6.0	5.6	4.7	14.7	11.5	10.0	11.5	7.0	6.1
7000	4.2	6.7	2.7	5.6	8.9	9.3	5.6	5.8	8.6	5.0	4.7	3.7	12.6	10.0	8.7	10.1	6.8	4.9

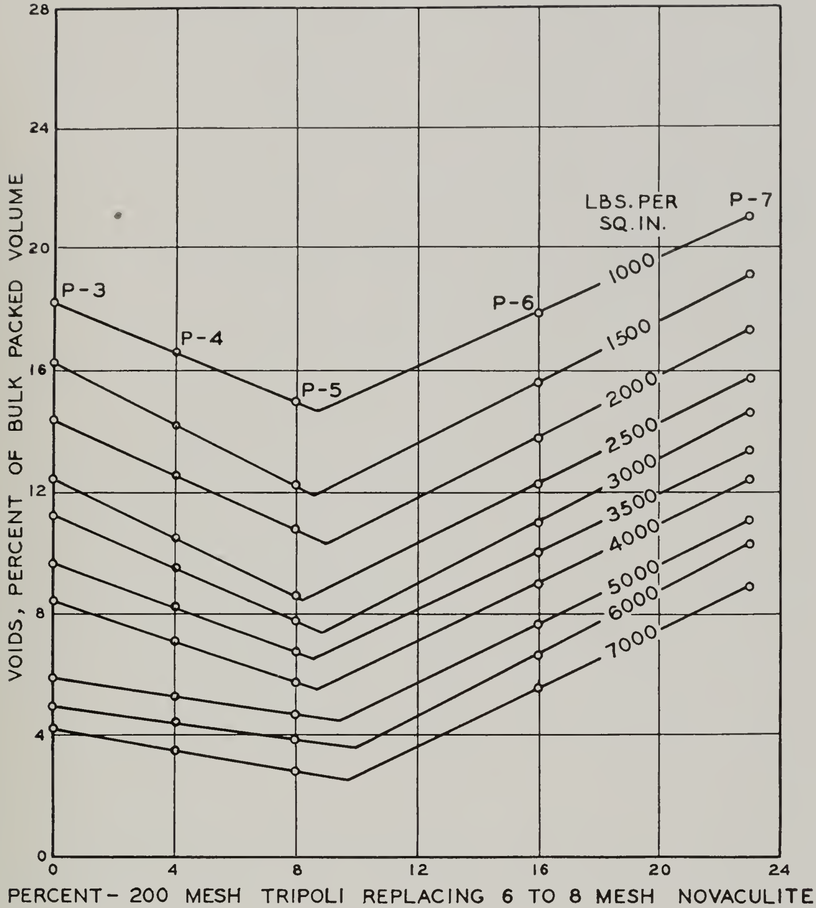

FIG. 5.—Packing of crushed mine-run novaculite by pressure.

parison of figures 5 and 6 shows two outstanding differences: The clay-free grains did not pack nearly so closely. P-3 packed to 18.2 percent voids at 1000 pounds per square inch pressure, whereas P-17 at the same pressure packed to 29.5 percent voids. The minimum voids for the clay-free grains was 8.2 percent at 7000 pounds per square inch, whereas the mine-run mixture had a minimum of 2.5 percent voids at the same pressure. The clay-free grains also required more fines to bring about the minimum void composition. The clay-free grains had a minimum at about 13 percent of the tripoli, compared with 9 percent for the mine-run samples. It appears that the clay acts as a lubricating medium during packing.

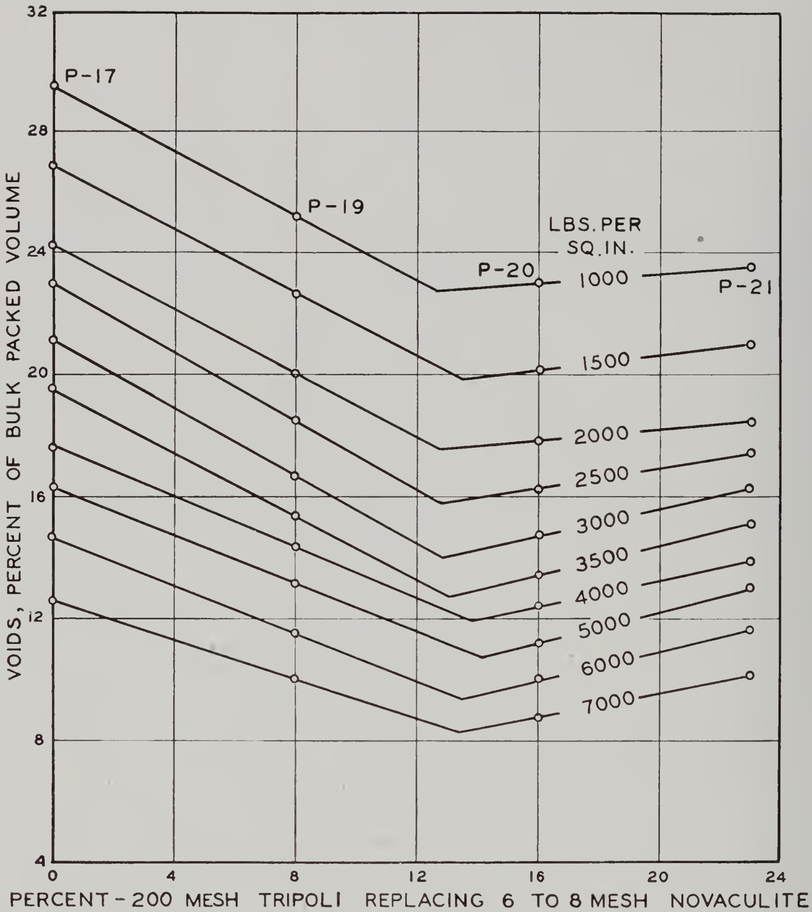

Fig. 6.—Packing of crushed washed novaculite by pressure.

Inversions of Silica

Reference has already been made to the fact that silica exists in several crystalline forms, each of which has its characteristic temperature range of stability. When the temperature to which any particular form is subjected is higher or lower than the stability range of a particular form, it inverts, or changes into the crystalline form peculiar to the new temperature conditions. These changes are of practical importance because each inversion is accompanied by a change of volume, expansion or contraction, and some are rapid and of considerable magnitude, others are sluggish and slight. A familiar example of the nature and effect of a rapid inversion of a form of crystalline silica is the shattering of a quartz pebble when strongly heated or the lack of strength in very sandy clays after they have been fired. Numerous other illustrations might be cited. The silica inversions which are of interest in this study are:

Inversions	*Temperature*	*Rate*
*Low to high-quartz	573 ± 1° C (1063° F.)	Rapid
High-quartz to upper high-tridymite	870 ± 10° C (1598° F.)	Sluggish
High-tridymite to high-cristobalite	1470 ± 10° C (2678° F.)	Sluggish

*Low-quartz is known as alpha-quartz, high-quartz as beta-quartz; upper-high-tridymite is also beta-tridymite; high-cristobalite is also beta-cristobalite.

The temperatures and rate at which the inversions take place in commercial operations are influenced by the fineness of the silica, the presence and the nature of impurities in the material, and the kind of flux or bonding agent employed, and the duration of the heating. The densities of the principal forms of silica are:

Low-quartz	2.65
High-tridymite	2.26
High-cristobalite	2.32

When the low-quartz inverts to high-tridymite there is a large volume increase; the inversion of the high-tridymite to the high-cristobalite is accompanied by an additional increase of volume. Quartz at 1200° C. has a density of about 2.55, while cristobalite at the same temperature has a density of about 2.2. An inversion then at, say 1200° C., will cause an increase in volume of about 15.9 percent, but the change from cristobalite to tridymite involves a volume change of less than 1 percent.

These are the volume changes that occur during heating. During cooling, if there is any untransformed quartz at 537° C., it will contract the same amount that it expanded. Over the range of about 200° C. to 250° C., cristobalite changes, in cooling, from a density of 2.225 to 2.29, a volume change of about 3 percent. Tridymite has two low-temperature inversion points, 117° C., and 163° C. The volume changes here are a fraction of one percent.

Silica brick expands permanently during firing, due to the change of quartz to cristobalite and tridymite, and the volume change may amount to as much as 15 percent but rarely reaches that figure. Therefore, as would be expected, the specific gravities of silica brick are good criteria by which to judge whether the brick has had proper heat treatment. As only 70 to 80 percent of the quartz is converted to cristobalite and 5 to 10 percent to tridymite in a commercial burn, a brick with a specific gravity of less than 2.40 is considered satisfactory. Much of the ware on the market has specific gravities of 2.30 to 2.35 and is decidedly superior to the ware of higher specific gravity.

Silica refractories are useful because of their rigidity at temperatures at which ordinary fireclay brick soften, and because they expand slightly when heated instead of contracting.

Rates of Inversion of Novaculite

experimental details

Method.—The study of the inversion rates was made by observing linear expansions at constant temperature. For this purpose an apparatus described by Chesters and Parmelee[5] was used. For the convenience of the reader a brief description of the apparatus is given here.

A fixed member, a 1.2-inch diameter alundum tube, OT, carried the entire expansion system. Slots were cut on either side of this tube so that the alundum shelf, B, could be inserted into the tube to support the specimen S. The specimen was separated from the shelf and from the moving push rod, PR, by platinum washers. The gage holder, GH, was a heavy brass head which was clamped to the outside tube OT, by screws, S. The push rod, PR, was capped with a stainless steel cap, C, which had been machined to a sliding fit in GH. A 1/10,000 inch Ames Dial, G, was attached to GH, as shown. A counter-weight of 300 grams was used to take the load off the tube. The specimens were made so that the thermocouple, T, could be inserted at their center. The furnace was a molybdenum wire wound furnace which has been described by Chesters and Parmelee.[6]

Specimen.—Thirty grams of novaculite of proper grain size was weighed out, then mixed with 2½ cc. of water and the desired amount of flux. This was then mixed for about 15 minutes with the fingers and placed in a mold (fig. 8). A uniform pressure of 2500 pounds per sq. in. was used in all tests. The test piece was 0.9 inch in diameter and 1½ inches in height. It had a hole in its center to accommodate a ther-

[5] Chesters, J. H. and Parmelee, C. W., The measurement of reaction rates at high temperatures: Jour. Am. Ceramic Soc., vol. 17, No. 3, pp. 50–59, 1934.

[6] Chesters, J. H. and Parmelee, C. W., The burning of magnesite brick: Trans. Ceramic Soc. (Eng.), vol. 32, No. 7, pp. 349–70, 1933.

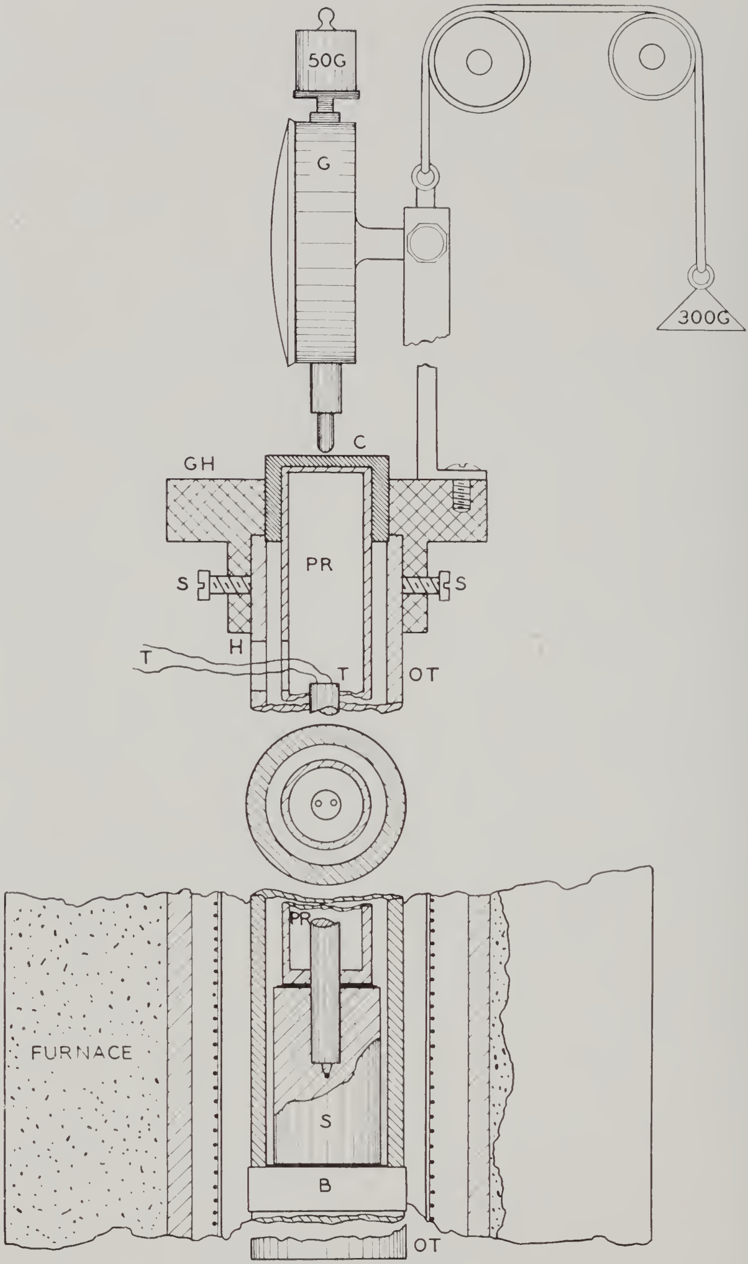

FIG. 7.—Thermal expansion apparatus.

mocouple, as shown in figure 7. After pressing, the samples were dried and stored in a dessicator. The test pieces were measured carefully with a 1/100 millimeter platform Ames dial device.

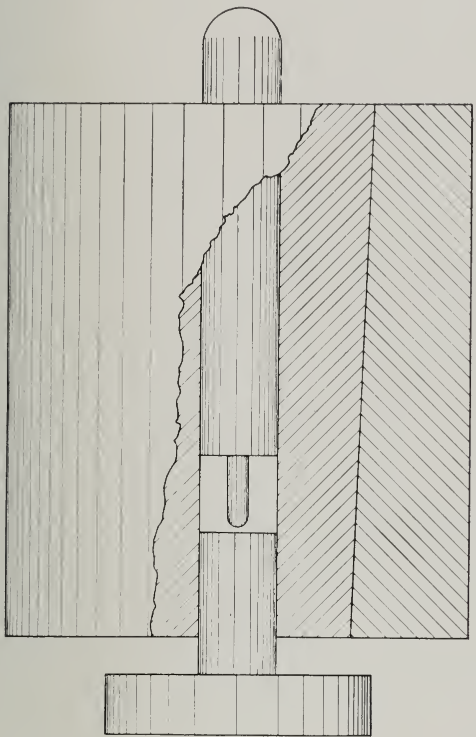

FIG. 8.—Mold for pressing samples.

Expansion measurements.—The apparatus was set up as shown in figure 7, and the furnace was well swept with hydrogen. When conditions were safe, the temperature was raised at an approximately linear rate of 23° C. per minute. When the desired temperature was reached, it was held constant at that figure until the completion of the test. Temperature and dial readings were taken every two minutes until changes occurred more slowly, when readings were taken at less frequent intervals.

Measurements on specimens after firing.—The porosity of the fired test pieces was measured by the suspended weight method, the samples having been saturated with water in a vacuum. Densities were determined by means of pycnometers. Water was added to the samples in the pycnometers in vacuo.

RESULTS

Method of representing results.—In the graphs which follow, expansion has been plotted against time. During the heating period, the temperature was proportional to the elapsed time, the heating rate being 23° C. per minute. The volume changes occurring during this period were not accurately determined, due to this fast rate of heating. The chief concern was the expansion at constant temperature. In every case the inversion was from quartz to cristobalite, and the expansion at constant temperature was caused by the inversion, together with other changes of physical structure.

The initial rapid expansion below 27 minutes (about 600° C.) was due to the thermal expansion of low quartz. The negative expansion which then occurred was too great to be due entirely to the negative thermal expansion of high quartz. The negative expansion has been found to continue until cristobalite is formed in appreciable quantities. The point at which constant temperature started is marked on each curve. Figure 9 has been prepared as a typical example of the method of representing the data.

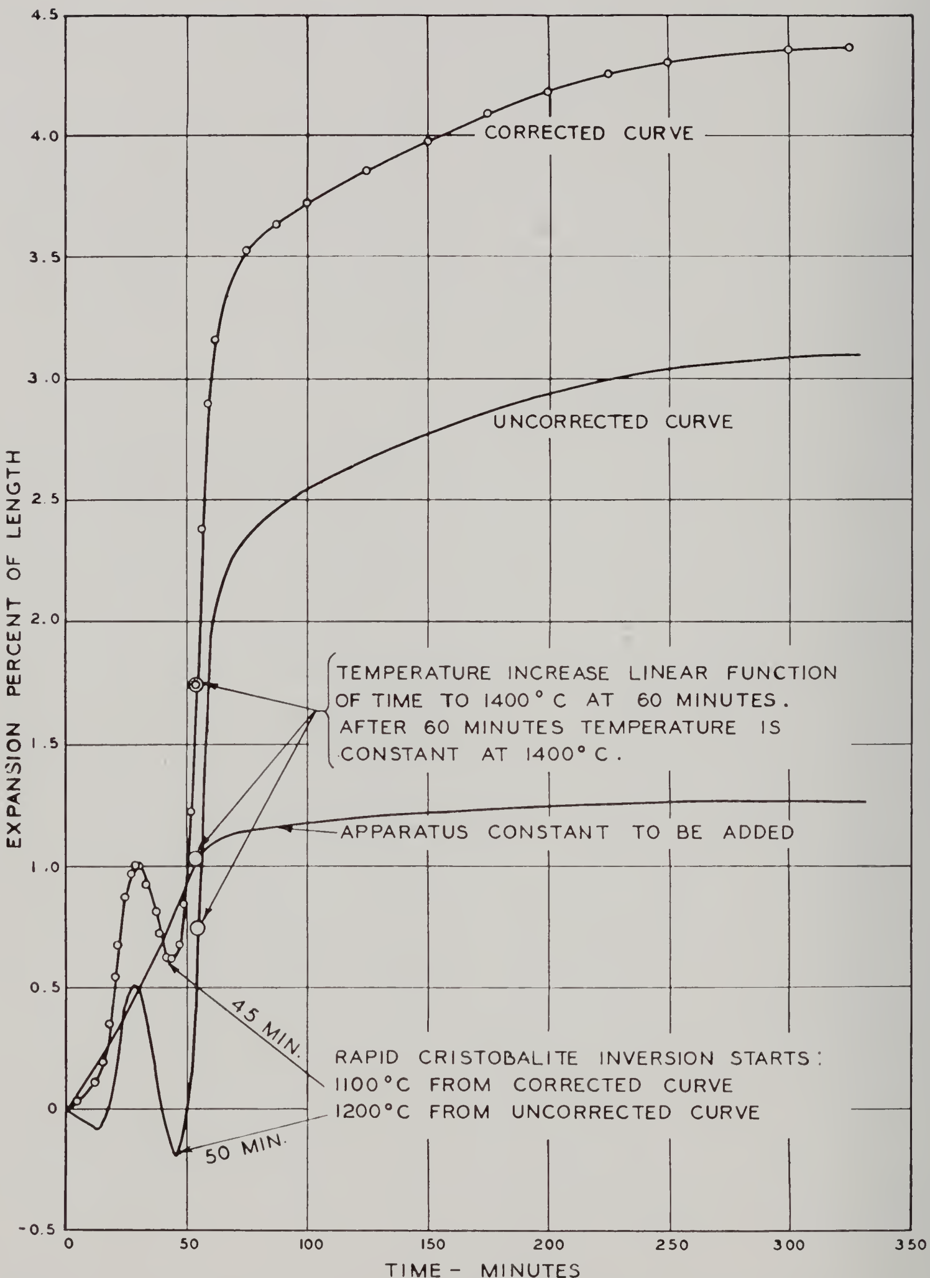

FIG. 9.—Graph illustrating the effect of the apparatus constant on the expansion-time curve of novaculite.

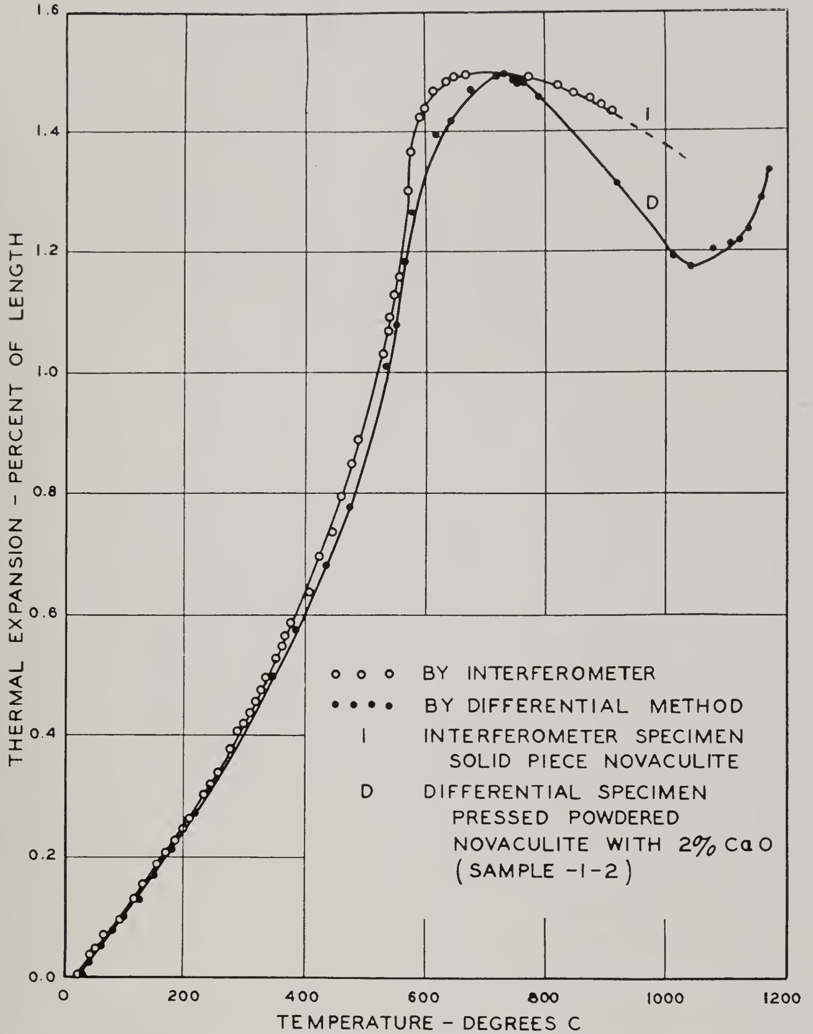

FIG. 10.—Comparison of data from interferometer and differential apparatus.

Comparison of data from interferometer and differential apparatus.—The interferometer is well known as an instrument of great precision for the measurements of thermal expansion. It was for this reason that it was used here as check on the differential apparatus. It was particularly desirable to make sure of the negative expansion above 600° C. For the interferometer test, samples were ground from clear solid novaculite. The rate of heating was 2° C. per minute. The results are shown in figure 10, curve I. The shrinkage above 700° C. was greater than that of high quartz. The cause of this shrinkage was not known for certain, but we have postulated that it is due to a reaction between the silica and its impurities. The chemical analysis shows a loss on ignition (probably combined water) of 0.62 percent which might account, in part at least for this shrinkage. The other impurities are MgO, 0.12 percent, Al_2O_3 1.16 percent, alkalies 0.11 percent, and Fe_2O_3 0.33 percent. Any sintering would have to be caused by one or more of these constituents.

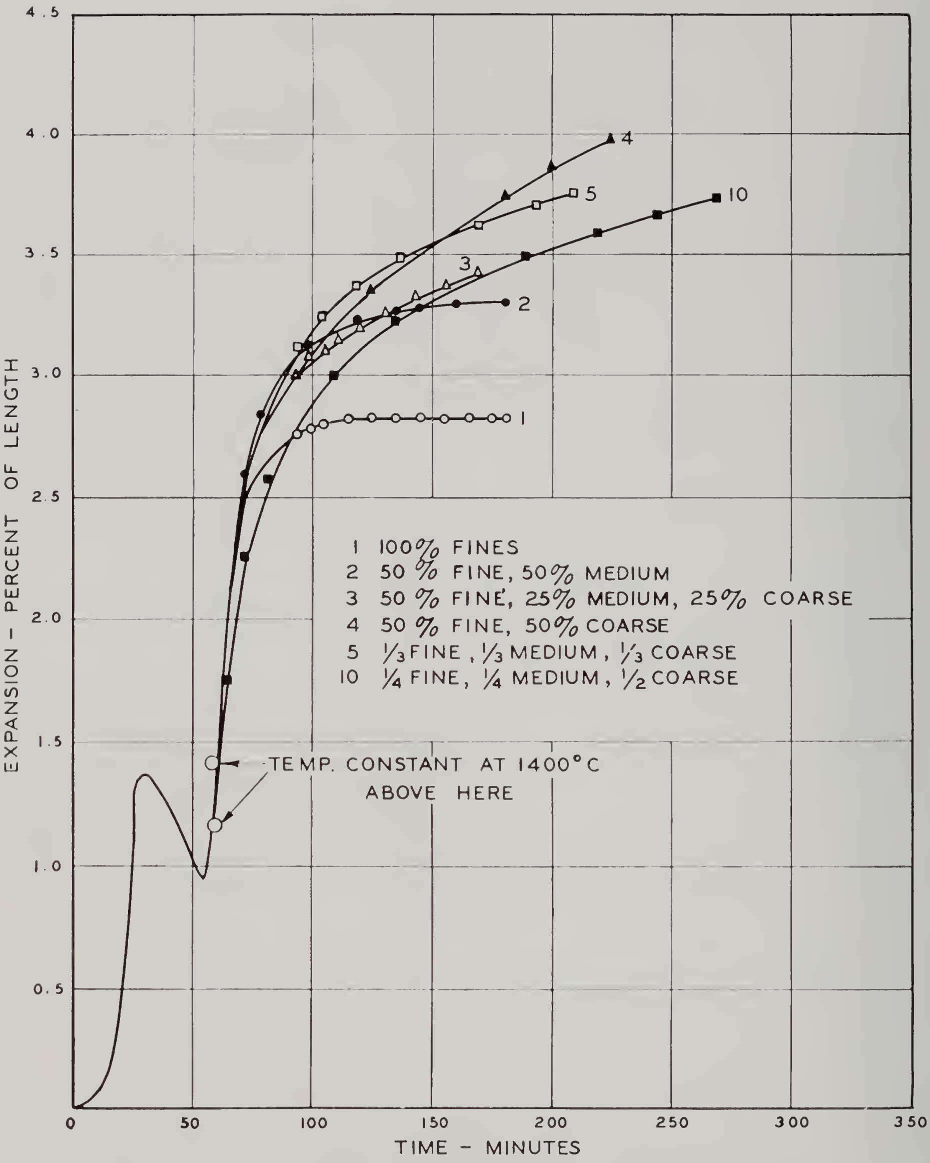

FIG. 11.—Effect of grain sizes on the rate of inversion of novaculite.

Curve D was determined with the differential apparatus on a sample of 200-mesh novaculite bonded with 2.0 percent CaO. Curves I and D are in substantial agreement, except that curve D shows a much greater shrinkage above 700° C. In this case positive expansion was again resumed at 1040° C. which indicates the inversion of quartz to cristobalite. This point would vary considerably, depending upon the rate of heating of the specimens.

Influence of grain size.—The following samples were made up of selected novaculite of different particle-size grading, bonded with 2.0 percent CaO. The grading was as follows:

No. 1. 100 percent fines.
No. 2. ½ fines, ½ medium.
No. 3. ½ fines, ¼ medium, ¼ coarse.
No. 4. ½ fines, ½ coarse.
No. 5. ⅓ fines, ⅓ medium, ⅓ coarse.
No. 10. ¼ fines, ¼ medium, ½ coarse.

The sieve size of the fines, medium, and coarse fractions were: through 200-mesh, through 28 on 48-mesh, and through 8 on 10-mesh, respectively. The results of the expansion tests have been plotted in figure 11. The initial and final porosities and the final densities are tabulated in table 6.

Table 6.—Densities and Percentage Porosities of Samples
1 to 5 and 10

Sample Number	Density 20° C	Porosity raw (percent)	Porosity fired (percent)
1......	2.35	38.4	38.4
2......	2.36	32.0	30.4
3......	2.36	25.9	28.2
4......	2.36	26.9	29.6
5......	2.36	25.9	26.9
10......	2.36	25.3	26.1

None of these expansions was great enough to account for the density changes observed. The specific gravities of the specimens after heating showed conclusively that the material had inverted largely to cristobalite, presumably about 85 to 90 percent. The expansion system was repeatedly checked to assure accurate results. The material undoubtedly shrank at the same time that the expansion due to inversion was taking place. The porosity values observed were not helpful in explaining the cause. The volume changes were the results of two or more phenomena. In most cases the effect has been due largely to the inversion of high-quartz to cristobalite.

Because of the lack of accurate information concerning all the volume changes that have taken place, the total amount of expansion cannot be interpreted specifically, but the shapes of the curves are important because they tell the rates at which these changes proceed.

Figure 11 shows that the finer grained mixes reached stability much earlier than the coarser grained mixes. Sample 1, composed of novaculite finer than 200-mesh, showed no further expansion after one hour at 1400° C. The total expansion was also very low, indicating that much sintering and shrinkage had taken place. This was also the strongest specimen of the lot. Sample 2, of equal parts of 200-mesh and 28 on 48-mesh material was similar to sample 1 but was still expanding slightly at the end of the test. The expansion was greater than in sample 1, but less than in the other samples. In general, an increase in size of grain slowed the inversion and increased the expansion. The final densities of the samples were all very much the same as shown in table 6. If the porosities had been properly measured, taking all factors into account, we should be able to interpret these changes more fully. Finer grains invert more rapidly, as may be seen from curves 1 and 2. It should be a safe assumption that most of the shrinkage and sintering was associated with the finest fractions. From the figure we may conclude that these changes were largely completed very soon after the maximum temperature had been reached. The continued expansion of samples 3, 4, 5, and 10 may then be assumed to be due to the inversion of the larger grains to cristobalite. Independent observation has shown that the larger grains after rapid inversion to cristobalite were soft and rather chalky and were no doubt full of many small pores, which suggested a shattering effect.

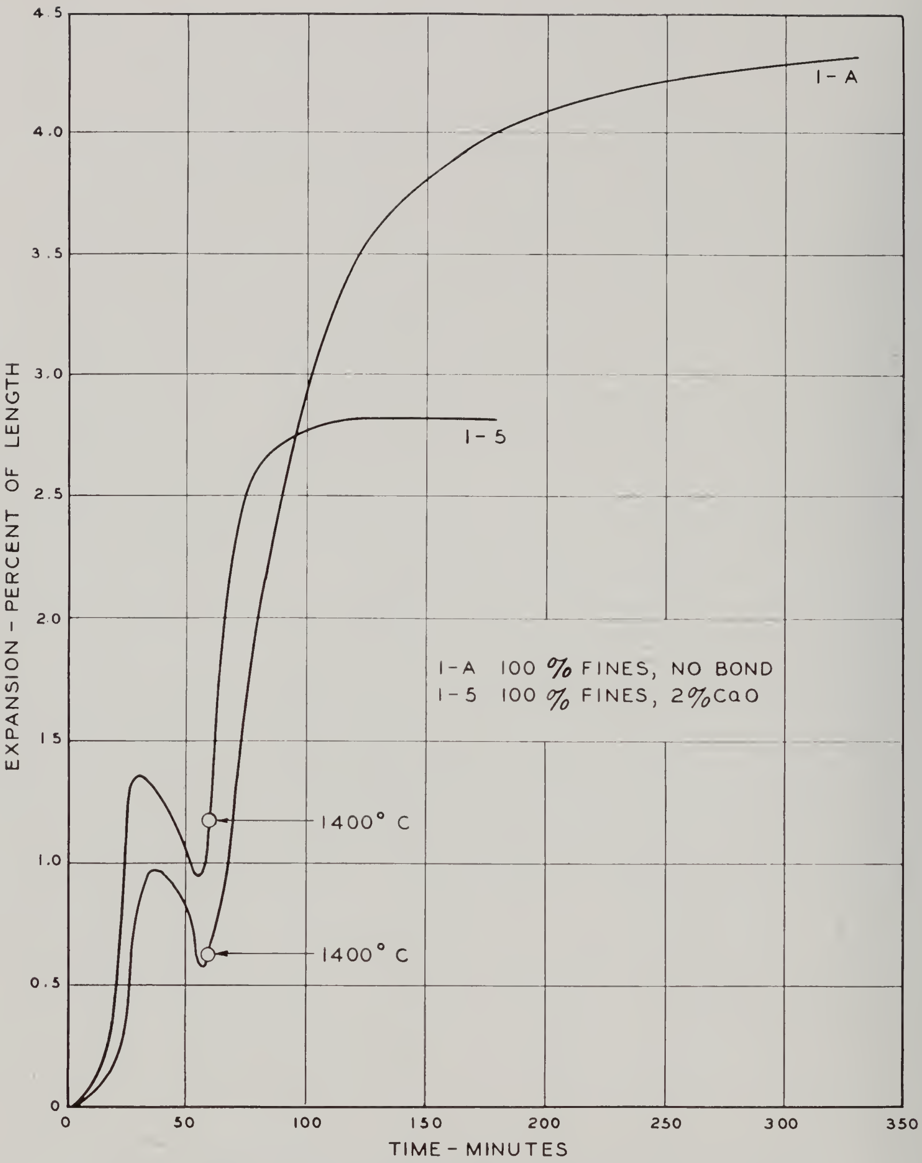

FIG. 12.—Effect of the use of bond on the rate of inversion of novaculite.

TABLE 7.—PERCENTAGE POROSITIES AND DENSITIES OF EXPANSION SAMPLES

Number	Flux	Porosity raw (percent)	Porosity burned (percent)	Density 26° C
F–1	3% CaO	26.3	28.1	2.35
F–2	3% Calcium phosphate	24.5	23.5	....
F–4	3% Fe_2O_3	26.7	32.0	2.36
F–4A	3% Fe_2O_3 as $Fe(OH)_3$	26.7	29.7	2.36
F–8	3% borax	27.4	33.7	2.30
F–8A	3% fused borax 80 mesh	26.7	32.1	2.29
F–8B	3% borax	33.5	34.0	2.32
F–13	Sodium tungstate	24.8	28.3	2.34
F–21	1½% borax+0.6% Fe_2O_3+0.6% CaO	27.1	31.4	....
F–22	1½% BaO+1½% B_2O_3	26.8	30.1	2.35
F–23	1½% BaO+1½% Fe_2O_3	24.7	27.0	2.35
F–24	2% CaO+1½% Fe_2O_3+1½% Na_2O	22.6	27.8	2.35
F–25	1% CaO+0.9% Fe_2O_3+0.9% Na_2O	20.4	31.0	2.34
F–26	1.2% BaO+0.9% Fe_2O_3+0.9% Na_2O	20.2	30.4	2.34

EFFECT OF VARIOUS FLUXES

COMPARISON OF VOLUME CHANGES IN SPECIMENS WITH AND WITHOUT BOND

The differences in volume changes between bonded and unbonded specimens is shown in figure 12. These were made of novaculite finer than 200 mesh, 1-5 was bonded with 2 percent CaO and 1-A was unbonded. Both samples inverted almost entirely to cristobalite. The lime-bonded sample reached a constant length after about 1 hour at 1400° C., whereas the unbonded sample was still changing after 4½ hours at the same temperature. The expansion of the lime-bonded specimen was much less than that of the unbounded sample. This was taken to mean that the sintering and consolidation processes were much greater in the presence of lime. Both samples showed the characteristic shrinkage above 600° C. The expansion, hence the inversion to cristobalite, began at a lower temperature in the presence of the lime.

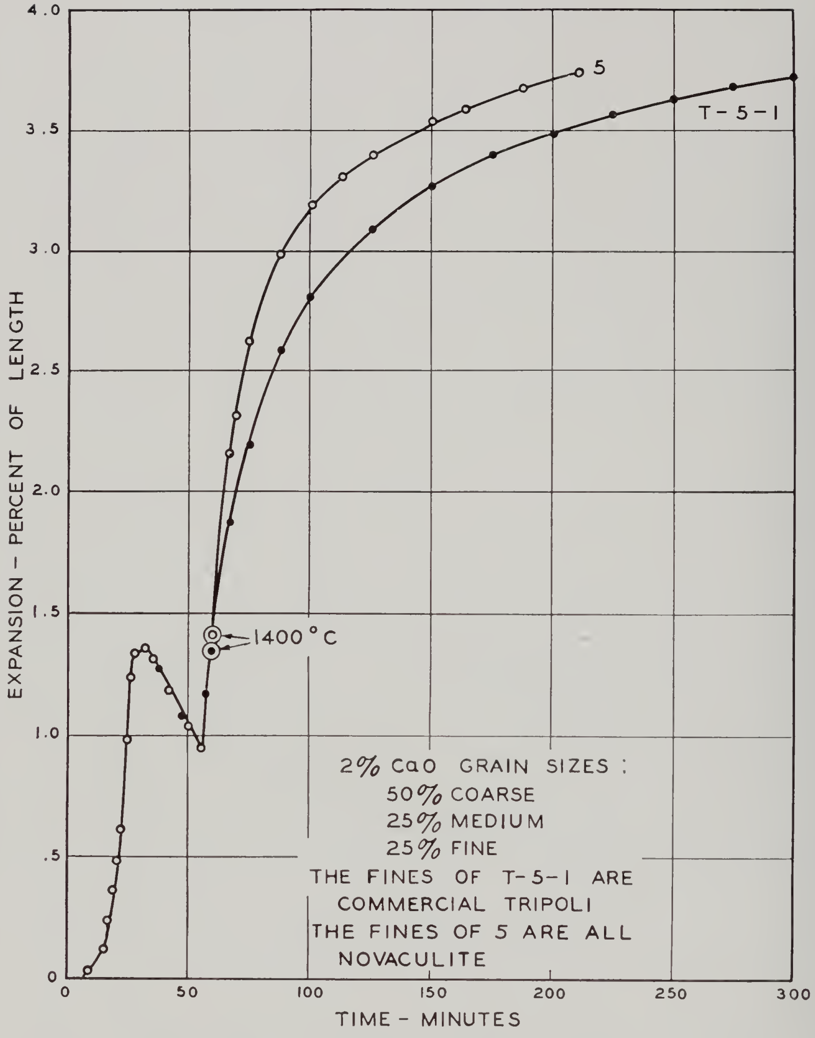

FIG. 13.—Effect of the use of tripoli on the rate of inversion of novaculite.

PARTICLE GRADING USED

The mixture of grain sizes used in all experiments given below in this section were 50 percent 8 to 10-mesh, 25 percent 14 to 28-mesh, and 25 percent 200-mesh. The finest fraction was composed of Illinois tripoli instead of powdered novaculite. The effect of the tripoli as compared with novaculite was very slight, as shown in figure 13. The body containing the tripoli as the fine fraction inverted somewhat more slowly than the all-novaculite body.

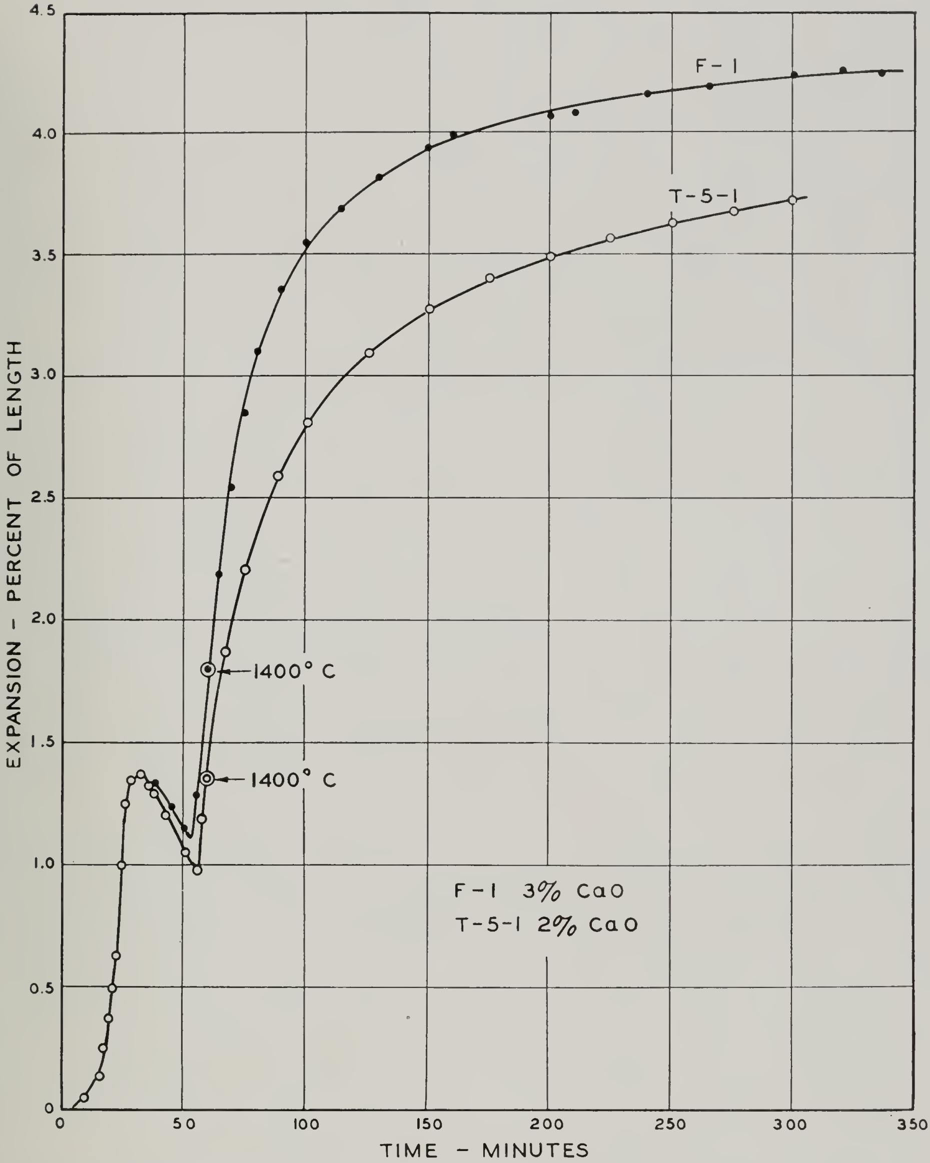

FIG. 14.—Effect of varying the amount of lime bonds on the rate of inversion of novaculite.

INFLUENCE OF THE AMOUNT OF BOND

The difference in rate of inversion between samples containing 2 percent and 3 percent CaO is shown in figure 14. It is evident that F-1 with 3 percent CaO inverted more rapidly than sample T-5-1, which was identical except that only 2 percent CaO was added. The difference in rate of inversion was only moderate. The final densities of the two samples were: F-1, 2.35 and T-5-1, 2.35. The inversion also started earlier in the presence of 3 percent CaO than in the presence of 2 percent CaO.

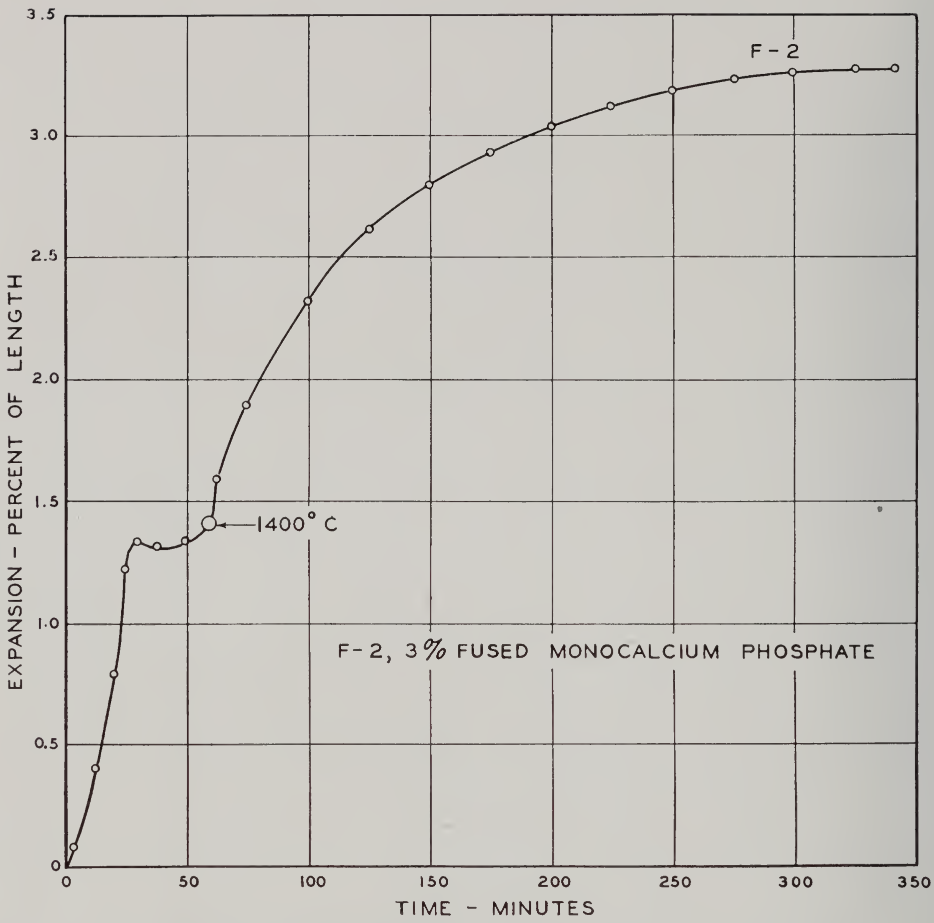

Fig. 15.—Effect of calcium phosphate on the rate of inversion of novaculite.

CALCIUM PHOSPHATE

Three percent fused monocalcium phosphate produced the result shown in figure 15. The rate of inversion is not as great as that produced by 2 percent CaO. There was a significant difference between the conduct of the two fluxes as shown by the forms of the graphs representing changes at about 600° C. Some action was at work in this sample which prevented the shrinkage in the high-quartz region characteristic of most of the other samples. Calcium phosphate cannot be said to be a good accelerator for this material.

SODIUM TUNGSTATE

Three percent sodium tungstate produced very rapid inversion as may be seen from figure 16. A considerable amount of the expansion observed on sample F-13 was thought to be due to the swelling of the flux during fusion. After about one hour at 1400° C., the temperature was raised to 1500° C., and no further expansion was noted. This was taken to mean that the inversion had become almost complete. Sample F-13MD was a sample of mine-run novaculite gravel containing 3 percent sodium tungstate which had been heated at

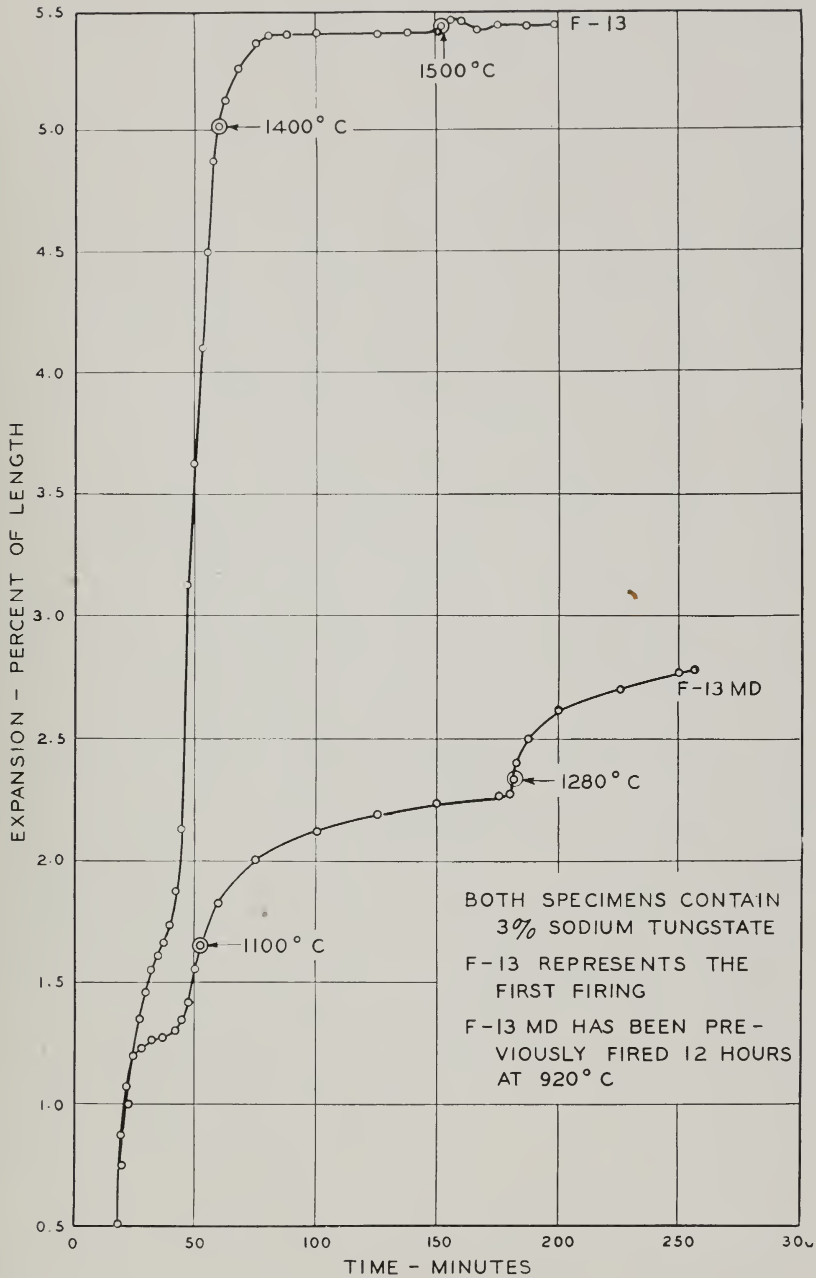

Fig. 16.—Effect of the use of sodium tungstate on the rate of inversion of novaculite.

920° C. for 12 hours. A similar sample after the same heat treatment had a density of 2.52, showing that some inversion had already taken place. This curve shows how the inversion decreases with time of heating at a given temperature. The sample was held at 1100° C. for about 125 minutes, then raised to 1280° C. At each temperature the expansion was rapid at first and gradually became progressively slower.

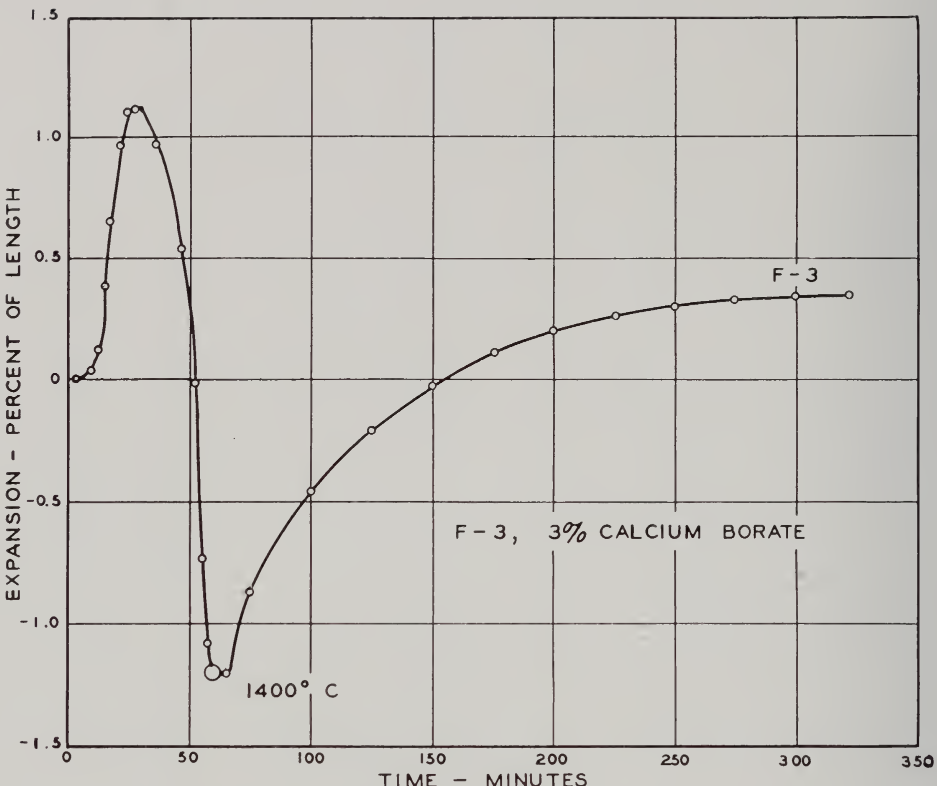

FIG. 17.—Effect of use of calcium borate on the rate of inversion of novaculite.

CALCIUM BORATE

When the flux used was 3 percent crystallised calcium borate an excessive shrinkage occurred above 700° C., an example of which is shown in figure 17. This specimen showed a net increase in length during firing of less than 0.4 percent.

BORAX

The effects of 3 percent borax on the rate of inversion to cristobalite at 1400° C., at 1300° C., and at 1200° C. is shown in figure 18. The borax was added to sample F-8 in solution. F-8A contained 80-mesh fused borax, and sample F-8B, 240-mesh fused borax. A comparison of the curves in figure 18 with those in figure 16 show that borax produced greater acceleration of the inversion than sodium tungstate. Sample F-8 was almost completely inverted before the temperature had reached 1400° C. Afterwards at a constant temperature of 1400° a small continuous shrinkage occurred. F-8B was held at a constant temperature of 1300° C., and the inversion proceeded about as rapidly as at 1400° C.

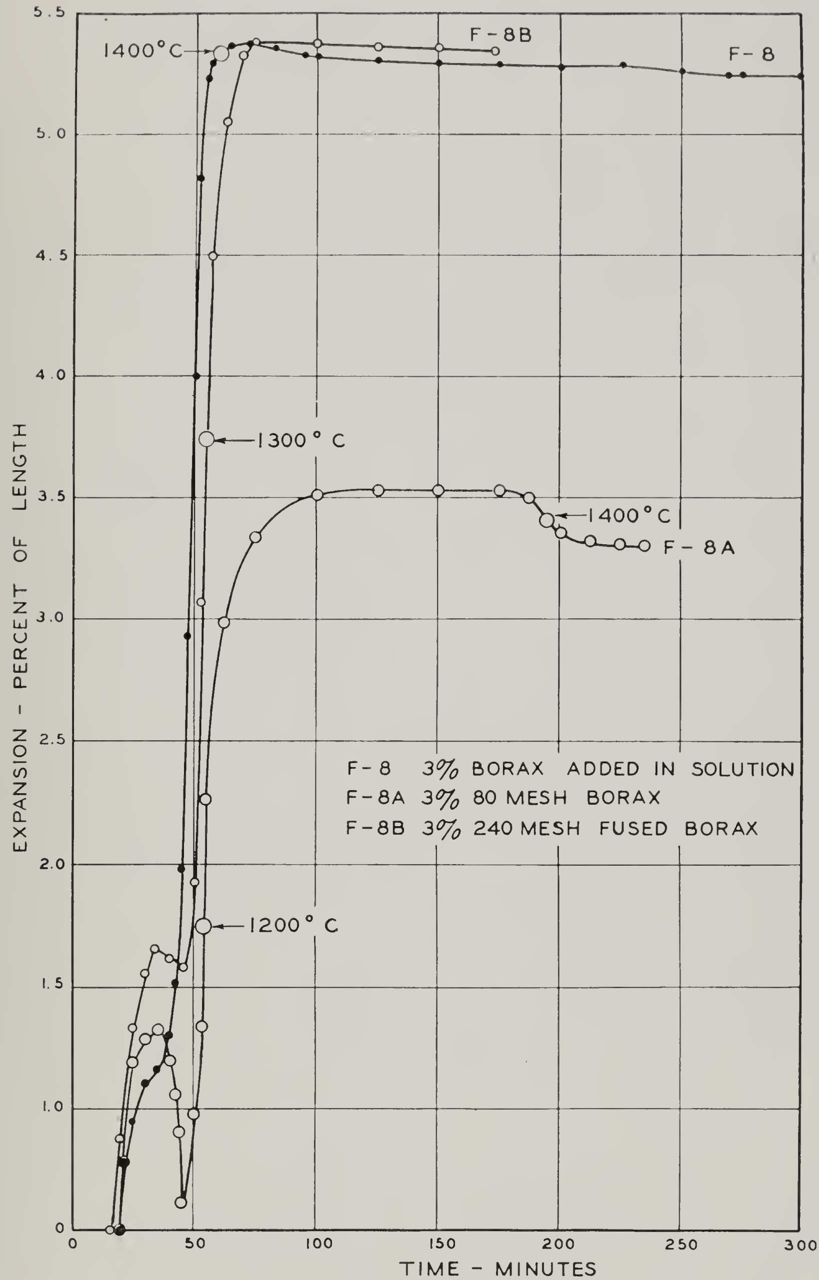

FIG. 18.—Effect of the use of borax on the rate of inversion of novaculite.

There was also a small shrinkage at constant temperature. Sample F-8A was held at 1200° C. and the specimen ceased to expand at the end of about one hour at this temperature. The inversion must have been complete, as no further expansion was observed when the temperature was raised to 1400° C. The density of this sample was found to be 2.29, showing lower density than any of the other samples in table 8.

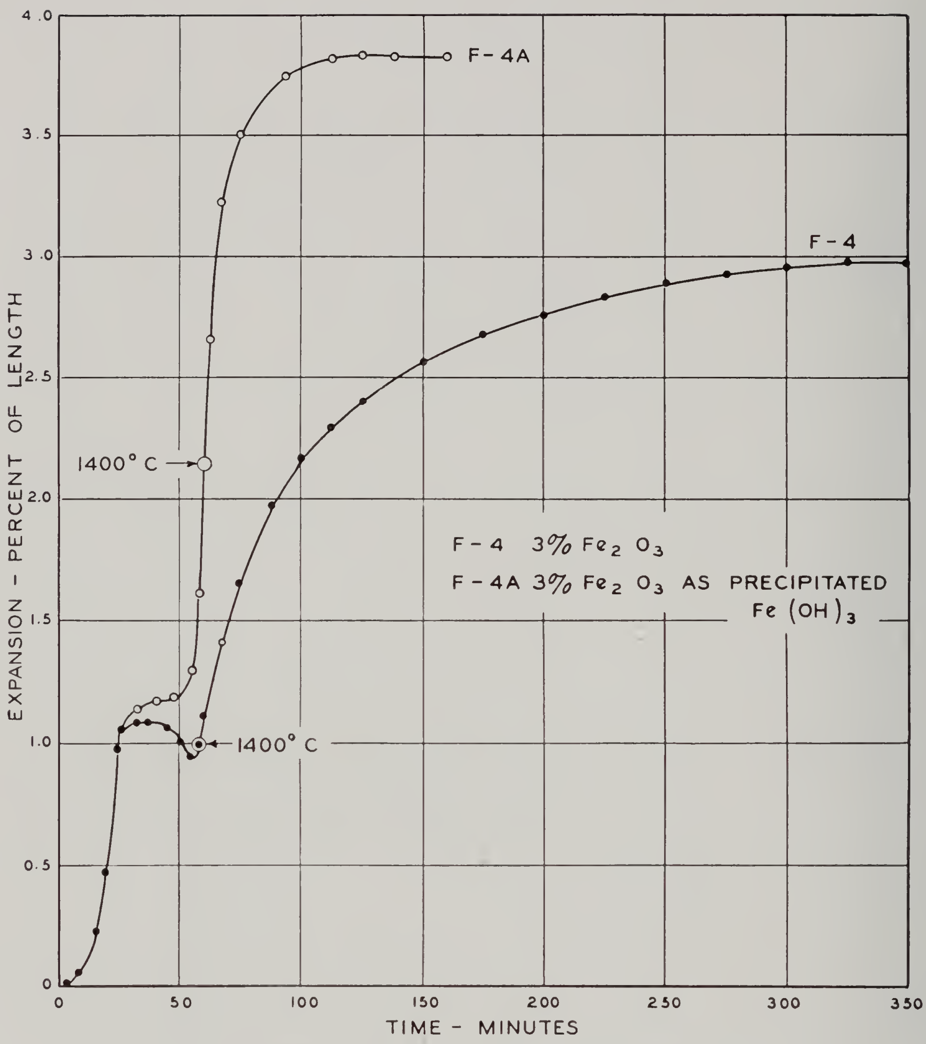

FIG. 19.—Effect of the use of ferric oxide on the rate of inversion of novaculite.

IRON OXIDE

Figure 19 shows the effect of the iron oxide upon the rate of inversion. Sample F-4 contained 3 percent pulverized c.p. Fe_2O_3. Sample F-4A was prepared by adding the 3 percent Fe_2O_3 as precipitated $Fe(OH)_3$. The precipitated iron was much more effective.

MIXED FLUXES

Sample F-21 (fig. 20) was composed of 1.5 percent fused borax, 0.6 percent CaO as $Ca(OH)_2$ in solution, and 0.6 percent Fe_2O_3 as c.p. iron oxide, making a total of 2.7 percent fluxes. The rate of inversion was very great but not equal to that when borax alone was used (fig. 18).

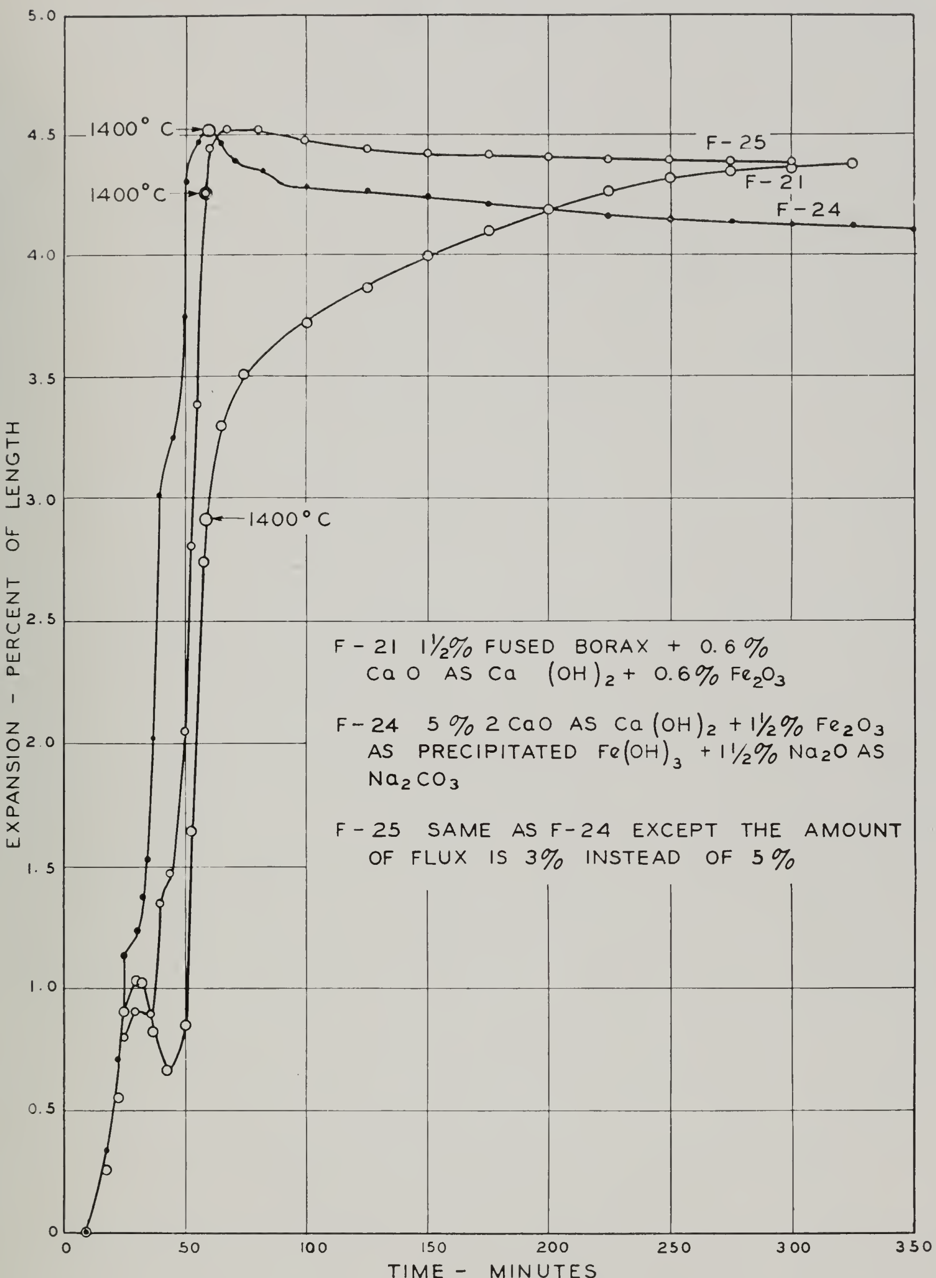

FIG. 20.—Effect of the use of mixed fluxes on the rate of inversion of novaculite.

The fluxes in samples F-24 and F-25 were prepared according to Salmang.[7] Sample F-24 contained 2 percent CaO as $Ca(OH)_2$ + 1.5 percent Fe_2O_3 as precipitated $Fe(OH)_3$ + 1.5 percent Na_2O as Na_2CO_3. Salmang added the flux in an insoluble form, which is to be preferred. F-25 was the same as F-24, except the amount of the flux was 3 percent instead of 5 percent.

[7] Salmang, H. and Wentz, B., Ber. Deut. Keram. Ges., 12, 1, 1, 1931.

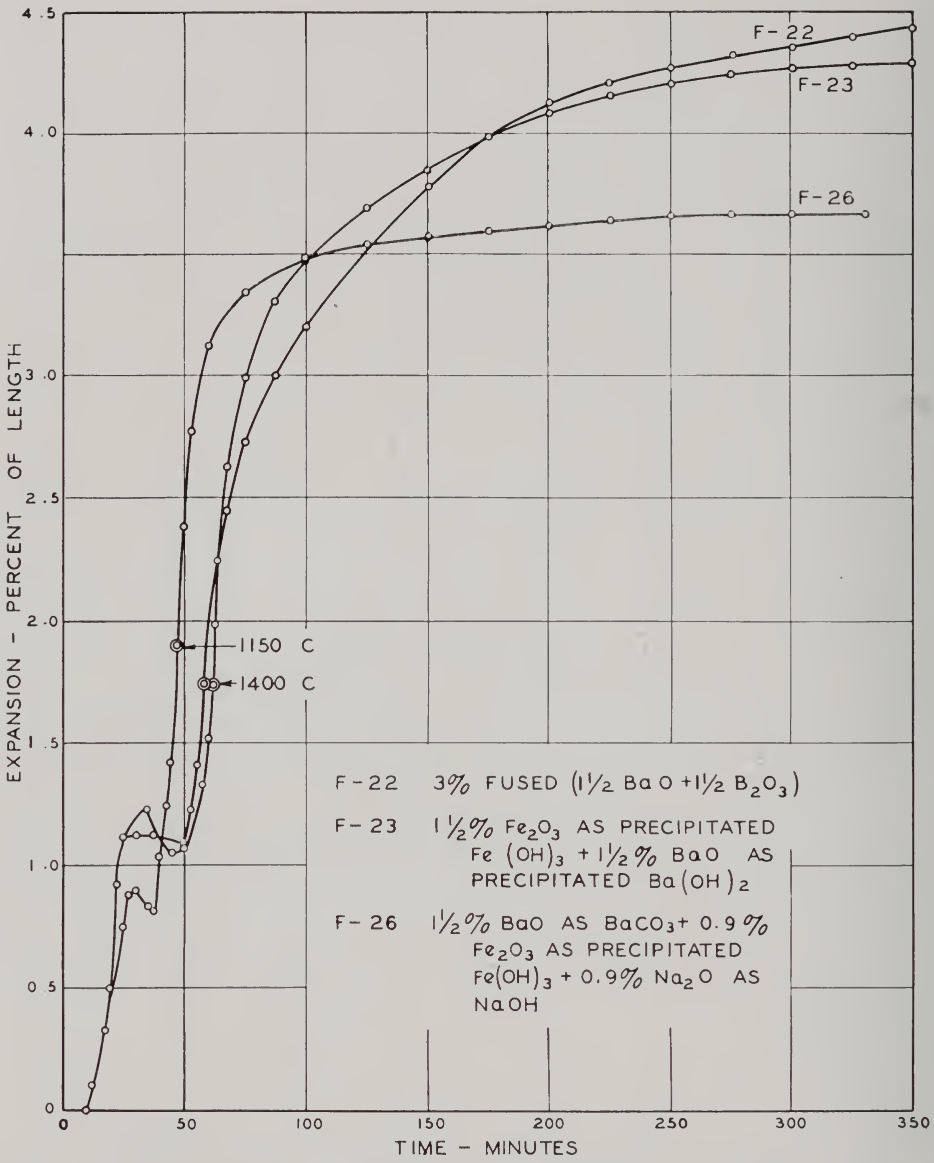

FIG. 21.—Effect of other fluxes on the rate of inversion of novaculite.

The expansion caused by F-24 was very rapid, and almost equal to that produced by borax. Continued shrinkage was observed at 1400° C., in samples F-24 and F-25.

Sample F-22 (fig. 21) contained a flux composed of 1.5 percent BaO and 1.5 percent B_2O_3, which had been fused and pulverized. Sample F-23 contained a flux composed of 1.5 percent BaO as $Ba(OH)_2$ and 1.5 percent Fe_2O_3 as precipitated $Fe(OH)_3$ There was not much difference between the behavior of these fluxes. The flux in sample F-26 was composed of 1.5 percent BaO as $BaCO_3$ + 0.9 percent Fe_2O_3 as precipitated $Fe(OH)_3$ + 0.9 percent Na_2O as NaOH. This sample inverted almost completely to cristobalite at 1150° C. in the time shown in figure 21.

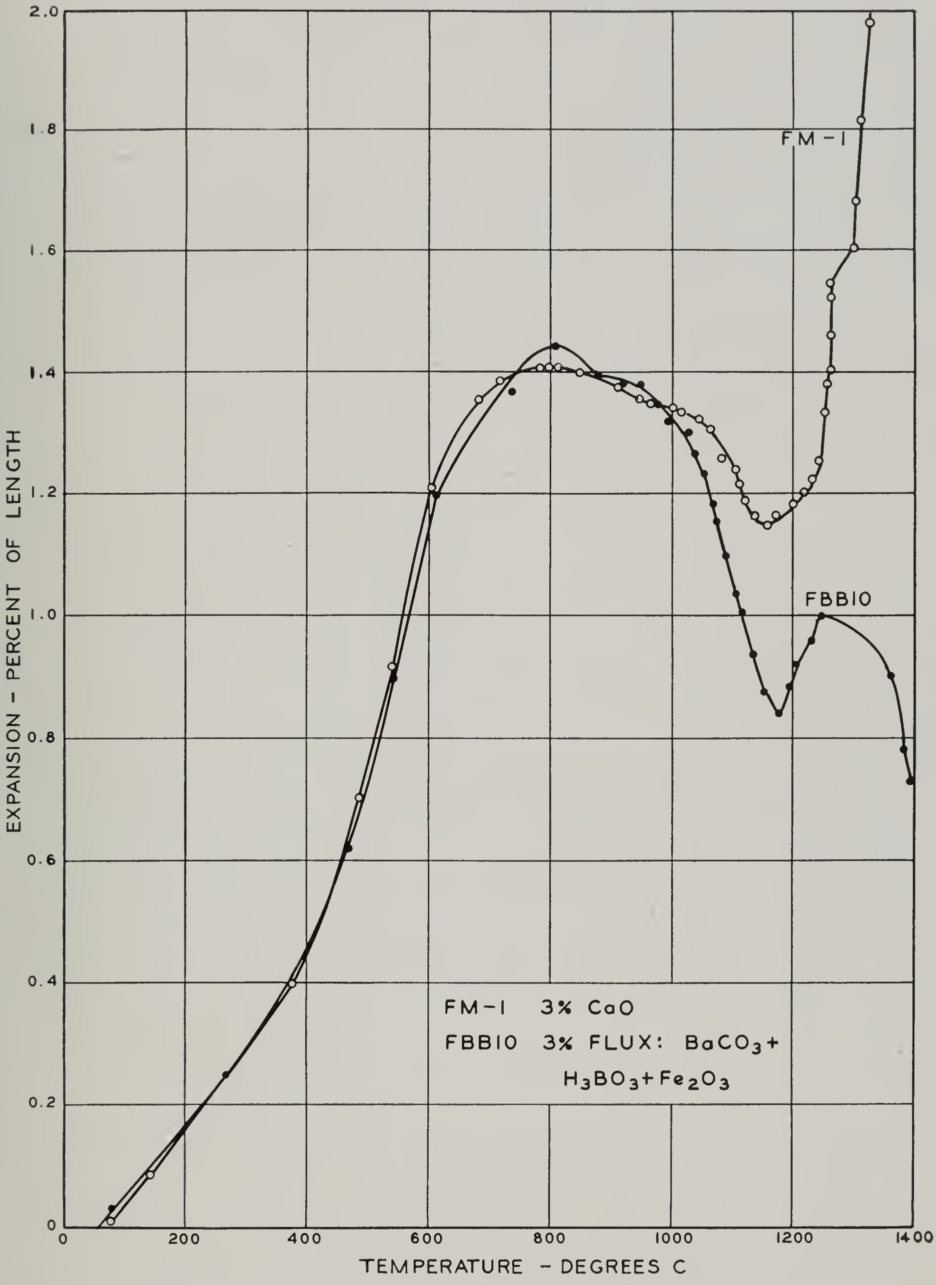

FIG. 22.—Graphs of expansion-temperature changes during firing of novaculite bodies.

EXPANSION TEMPERATURE CURVES OF UNFIRED NOVACULITE BODIES

Thermal expansion studies were made of two samples, employing a very slow heating rate. The curves are shown in figure 22. The samples were made of the same grain-size grading that was used for the compression tests described on page 41. Sample FM-1 was 97 percent novaculite and 3 percent CaO. Cristobalite began to be formed rapidly at 1150° C. Sample FBB-10 contained 3 percent bond that was a fusion of the following mixture: 130 grams Ba CO_3, 177 grams H_3BO_3 and 100 grams Fe_2O_3. This shrinkage in the high-quartz region was greater than with the lime-bonded sample, and was continuous except for a slight expansion between 1180° C. and 1250° C. due to cristobalite. The specimen was heated to 1500°, but the shrinkage still continued. This presumably was the differential of a simultaneous expansion due to cristobalite formation and a shrinkage due to the flux. It is conceivable that a proper blend could be made such that the specimen would show little volume change above 700° C. The specimen was very hard and dense after heating. It probably softened at the high temperatures. If this bond reduces the refractoriness of the silica, smaller percentages of it should be used.

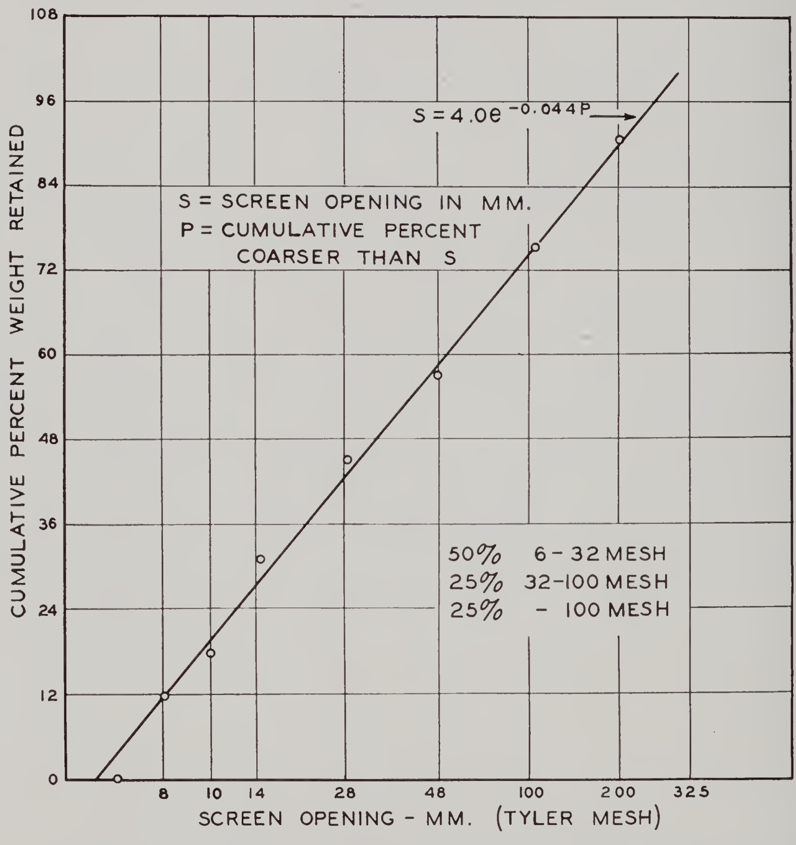

Fig. 23.—Distribution of particle size on grinding mine-run novaculite. 140 lbs. ground 40 minutes in wet pan (dry); tailings (on 6-mesh) 8.7 percent.

Preliminary Small-Scale Tests on Fabricated Samples

preparation of test samples

Grain size.—The rock was ground in a wet pan until the distribution of sizes was that shown in figure 23. The same grading was obtained from both the mine-run novaculite gravel and selected novaculite. Fine clay was present in the mine-run novaculite gravel but not in the selected novaculite. This grain sizing was chosen because it produced a good dense brick and because it could be easily duplicated. The correct grading for commercial use would have to be obtained by trial, in additional experiments.

Table 8.—Compressive Strengths of Novaculite Briquets $1\frac{1}{4}$ by $1\frac{1}{4}$ by $2\frac{1}{2}$ Inches

Number	Material	Bond	Compressive strength—lb. per sq. in.			
			Test 1	Test 2	Fired in No. 1 re-fired in No. 2	Test 3
OM	Mine-run**	None	1100	1300	1280	1960
OP	Selected†	None	590	610	640	820
P-11	Selected	1% CaO	....	....	....	950
P-12	Selected	2% CaO	....	....	....	1200
P-1	Selected	3% CaO	1260	1840	1900	1600
1-3M	Mine-run	3% CaO	1570	2040	2100	1120
M-4	Mine-run	$2\frac{1}{4}$% CaO+$\frac{3}{8}$% BaO+$\frac{3}{8}$% Fe_2O_3	2020	2680	2660	2860
P-5	Selected	$1\frac{1}{2}$% BaO+$1\frac{1}{2}$% Fe_2O_3	1750	2650	2230	....
M-6	Mine-run	2% CaO+1% FB10*	1890	2980	2700	2350
P-7	Selected	2% CaO+1% FB10*	1970	3450	3570	1930
P-8	Selected	2% CaO+$1\frac{1}{2}$% Fe_2O_3+$1\frac{1}{2}$% Na_2O	1770	2500	....	....
M-15	Mine-run	3% Feldspar	1360	1930	2380	2020
M-16	Mine-run	3% Anna Kaolin	870	....	1000	....
P-17	Selected	1% CaO+1% FB10*	....	....	....	1670
M-19	Mine-run	$1\frac{1}{2}$% BaO+$1\frac{1}{2}$% B_2O_3	1030	1420	1400	1750
X	From Commercial brick	?	2600	....	2710	1910

*FB10 was prepared by fusing the following mixture: 130 grams $BaCO_3$, 177 grams H_3BO_3, and 100 grams Fe_2O_3.
**Mine-run novaculite gravel.
†Novaculite.

Mixing of the bond with silica.—Ten pounds of batch was put in a bucket and the bond (in aqueous suspension) was poured on the same. The whole was made to a good slop-mold consistency by stirring for twenty minutes.

Forming the test pieces.—A wooden mold was used in which six $1\frac{1}{4}$ by $1\frac{1}{4}$ by $2\frac{1}{2}$-inch test specimens could be formed by throwing the wet mix into the mold with considerable force. The excess was then struck off with a spatula and the briquets were removed by inverting the mold and taking it apart.

Bonding agents used.—Various bonds, shown in table 8, were used in order to determine their effect on the cold compressive strength of the fired briquets. Each bonding material (table 8) was mixed as a slurry and added in the proper quantity. Since it was not believed possible to obtain as good mixing in the small quantities used as would be obtained in a wet pan, 3 percent of the flux was used instead of the customary 2 percent.

Firing the samples.—The samples were fired in the laboratory test kilns according to heating schedules shown in figure 24.

From inspection of samples after thermal expansion tests it was evident that the greatest cause of weakness in novaculite bricks was the too rapid inversion to cristobalite. Trials were made to determine the temperature limits at which this inversion should take place. The rather rapid increases in temperature to cone 14 in firings Nos. 1 and 2 were made with the idea that if inversion were substantially complete, it would not weaken the brick. If much uninverted quartz remained, the brick would have been "punky" and weak.

TESTING THE FIRED SAMPLES

Compressive strength tests.—Cold compressive strengths were determined on the $1\frac{1}{4}$ by $1\frac{1}{4}$ by $2\frac{1}{2}$ inch samples. The ends were set in plaster and the samples were broken in a hydraulic press.

Density measurements.—The densities of many of the samples were determined in order to obtain an index of the amount of

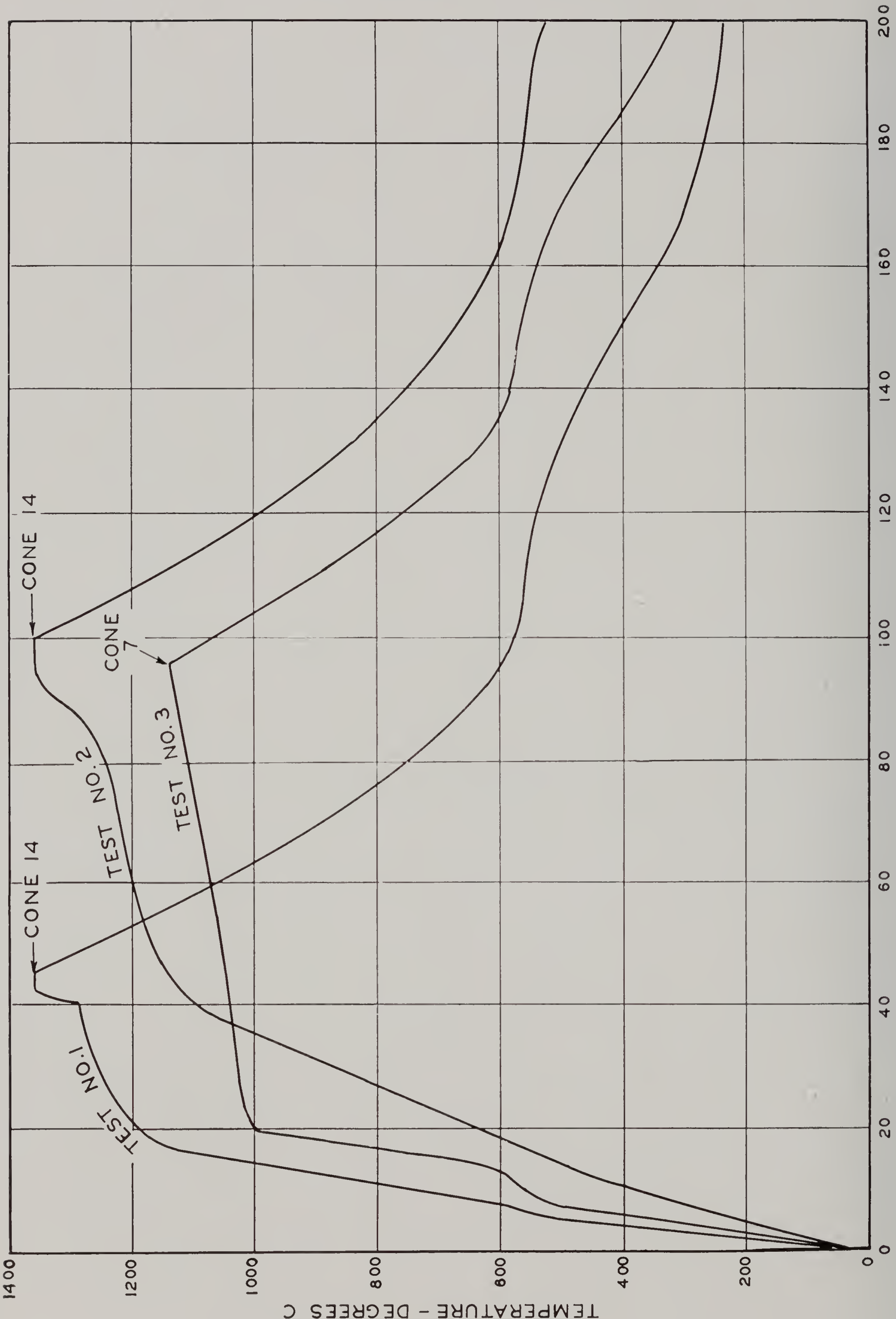

FIG. 24.—Heating schedules for firing novaculite brick samples.

inversion to cristobalite that had taken place. These measurements were made carefully with pycnometers, using very finely ground samples which had been wetted under a vacuum.

RESULTS OF FIRING TESTS

Table 8 shows the effects of the composition of the bond and the heat treatment on the compressive strengths. The heat treatment of these samples is shown in figure 24. The figures in the third vertical column of table 8 show the effect of refiring samples from test No. 1 in test No. 2. In every case the strength was substantially increased by this treatment. The samples from firing No. 2 were in every case stronger than those from firing No. 1. Some of the refired brick were stronger after the second firing than those of No. 2, but in general, the strengths were substantially the same. Those stronger after this treatment were P-7 and M-15; P-5 was weaker. With one exception, test No. 2 gave stronger brick than No. 1 because of the longer, more gradual fire, and firing No. 3 produced the weakest brick because the temperature was not high enough to develop the bond properly. The mine-run novaculite gravel without bond and containing its associated clay had maximum strength at the low temperature fire. The sample bonded with feldspar also had a good strength when fired to cone 7.

Aside from the heating-up period, which is too rapid for commercial size brick, the desired rate of heating novaculite for silica brick would be between firing Nos. 2 and 3. Firing No. 3 did not go to nearly high enough temperature to develop the bond and the tridymite, but the inversion was slow enough at that rate to prevent damage to a full-size brick. The inversion of the silica in fire No. 2 was too rapid and full-size brick were "punky." In these tests no attempt was made to produce the desirable network of tridymite crystals which develop in time at a high temperature. It is probable that there was some tridymite in some of the specimens, although not in sufficient quantities. The rate of heating should be

TABLE 9.—TRUE DENSITIES OF FIRED BRIQUETTES

	Test No. 1	Test No. 2	Fired in Test No. 1 Refired in Test No. 2
OM	....	....	2.29
OP	....	2.36	....
M-19	2.34	....	....
P-1	....	2.32	2.32
1-3M	....	....	2.32
M-4	....	....	2.34
P-5	2.32	2.31	....
M-6	2.31	....	2.33
P-7	....	....	2.32
M-15	....	....	2.29
M-16	....	....	2.30

very slow when inversion first begins and the rate may be gradually increased after that.

The composition of the bond was an important factor in the development of cold compressive strength. Pieces cut from unfired commercial silica brick and then fired in the same kiln were used for comparison. The lime-bonded novaculite brick were not as strong as the commercial silica brick. The cold strength of some experimental brick made with other bonds was much greater than the commercial brick which was lime bonded. The strongest brick was P-7, which was selected novaculite bonded with 2 percent CaO + 1 percent of a fusion of the following mixture: 130 grams $BaCO_3$, 177 grams H_3BO_3 + 100 grams Fe_2O_2. The average compressive strength of briquets of this composition was 3570 pounds per square inch.

Another very good quality brick was M-4 which was bonded with 2¼ percent CaO + ⅜ percent Fe_2O_3 + ⅜ percent BaO. The frits used in samples P-8 and M-19 were too soluble, which prevented their satisfactory test. On the whole, the use of BaO or BaO + Fe_2O_3 + B_2O_3 gave a distinct advantage in raising the mechanical strength of the brick.

It is known that Al_2O_3 is harmful to the refractoriness of a silica brick. Sosman[8] says this oxide should not exceed 2½ percent of the total and it should probably be

[8] Sosman, R. B., The properties of silica: Chem. Cat. Co., 1927.

lower than that. The Al_2O_3 in all these samples was much lower than this except M-15 and M-16. Other tests should be made on brick having these novel bonds before their use can be fully evaluated.

The specific gravities of some of the specimens are shown in table 9. They indicate a very high degree of inversion.

SUMMARY

Novaculite may be ground to give the grain sizes required to produce the desired structure of a brick. Tripoli may be added to increase the amount of fines. The total volume of voids accompanying the packing of novaculite grains decreases with decreasing grain size.

The grain-size distribution affects the rate of inversion to cristobalite and the amount of total expansion during firing. The finest grained mixtures invert the most rapidly and expand the least. In firing a novaculite brick, a shrinkage occurs above 600° C. which continues until cristobalite begins to be formed. This is assumed to be due to sintering and solid state reactions.

The bond serves a double purpose, that of drawing the grains into a compact mass and that of accelerating the inversion. The composition of the bond affects the rate of inversion and the temperature at which it begins.

Borax accelerates the inversion to cristobalite more than any other flux used. A little BaO replacing part of the CaO has a beneficial effect. Fe_2O_3 when added in a finely divided form is a good fluxing agent. The amount of total shrinkage is dependent to a large degree upon the kind of flux and the form in which it is added.

Novaculite briquets may be made which have superior compressive strengths. The replacement of some of the CaO with BaO, Fe_2O_3, or B_2O_3 greatly increases the cold crushing strength of novaculite bricks.

In firing novaculite, the temperature should increase 20° or 30° C. per day from 1000° C. for about three days, after which the rate should be increased slightly.

PART II—PREPARATION AND PROPERTIES OF SILICA BRICK MADE FROM ILLINOIS NOVACULITE AND QUARTZITIC SANDSTONE

Introduction

The purpose of this part of the work was to study the characteristics of novaculite brick with respect to (1) the preparation of the raw material, (2) fabrication, and (3) the finished product. In addition to novaculite, some tests have been made on a quartzitic sandstone from Tansil, Illinois. Where necessary, the properties of the Illinois material have been compared with those of commercial products.

Preparation of Material for Testing

NOVACULITE GRAVEL

Novaculite at the pit.—Overlying the hard compact massive novaculite are many feet of novaculite gravel containing a small amount of red clay. The gravel fragments are not rounded, as true gravel, but are angular and sharp edged. The screen analysis of the novaculite as received is shown in table 10.

Table 10.—Screen Analysis of Novaculite Gravel, "as received"

Particle size, sieve mesh	Wt. percent
Plus 1-inch	7.8
1 to ⅜-inch	29.2
⅜ to ¼-inch	22.2
¼ to 6 mesh	19.9
6 to 10 mesh	3.3
10 to 20 mesh	2.6
Minus 20 mesh	15.0
Total	100.0

Washing of novaculite gravel.—In the laboratory the gravel was placed on a 20-mesh screen and the clay and minus 20-mesh material was washed away by a stream of water. Twelve percent of material was washed through a 28-mesh screen. Table 11 shows the screen analysis of the mine-run gravel after washing.

Table 11.—Screen Analysis of "as received" Novaculite Gravel after Washing through 20-mesh and 28-mesh screens

Particle size, sieve mesh	Wt. percent
Plus 1-inch	8.8
1 to ⅜-inch	33.2
⅜ to ¼-inch	25.2
¼-inch to 6 mesh	22.6
6 to 10 mesh	3.8
10 to 20 mesh	3.0
Minus 20 mesh	3.4
28 mesh	12.0

SAMPLING FOR TESTS

Three hundred pounds of the novaculite gravel was washed, dried, thoroughly mixed, and stored for later use. Four hundred pounds of the novaculite was crushed to lumps one inch in diameter or less, mixed, and stored. It did not require washing. The quartzitic sandstone occurs in thick deposits of massive rock. Three hundred pounds were crushed to lumps one inch in diameter or smaller, mixed well, and stored without any further treatment.

PROPER GRAIN-SIZE DISTRIBUTION

Preparation of the material.—Three 125-pound batches of washed novaculite gravel were ground separately for 10 minutes each in a wet pan. Each lot of crushed material was then divided, by screening, into three grain-size groups. These groups were:

Coarse—on 14-mesh
Medium—Through 14-mesh on 100-mesh
Fine—Through 100-mesh

The relative amounts of each fraction obtained were: coarse 29.8 percent, medium 34.7 percent, and fine 35.5 percent.

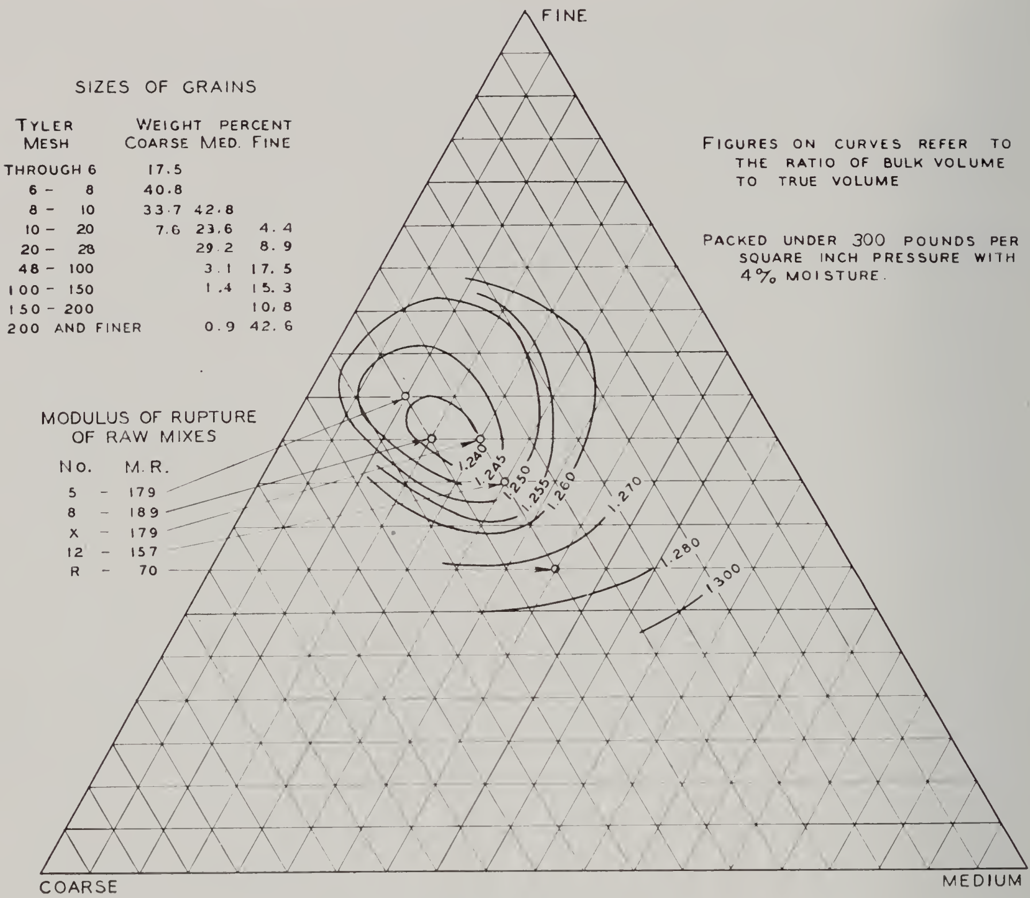

Fig. 25.—Packing of many grain sizes.

ADDITIONAL PACKING EXPERIMENTS

Method.—A mold of uniform circular cross-section was charged with 30 grams of grain mixtures, which had been moistened with 2 cc. of water. The charge was then packed by a piston with the application of a pressure of 3000 pounds per square inch. The volume of packed grains was calculated from the height of the piston after packing.

Grain sizes studied.—Various mixtures of the coarse (on 14-mesh), fine (through 100-mesh), and medium (through 14-mesh on 100-mesh) fractions, were packed. The screen analyses of these fractions are shown in table 12.

Results of packing tests.—The results of these tests are shown in figure 25. The values plotted were the ratios of the bulk volumes to the true volumes. The lines on the diagram represent mixtures which pack to the same density. From the plotted data it may be seen that 35 percent of the coarse, 15 percent medium and 50 percent fine (fractions identified in table 12) is representative of the densest packing mixture of this system. The grain-size distribution of this mixture, as calculated from the end members in the system, is shown in table 13. When this mixture was moistened with 4 percent water and pressed under a pressure of 3000 pounds per square inch, the resulting porosity was 19 percent.

Table 12.—Screen Analysis of the Ground Washed Mine-run Novaculite Gravel Divided into Three Fractions
In percent

Sieve mesh	Coarse	Medium	Fine
Plus 6	17.5	....	....
6 to 8	40.2	....	....
8 to 10	33.7	....	....
10 to 20	7.6	42.0	....
20 to 28	....	23.6	4.4
28 to 48	....	29.2	8.9
48 to 100	....	3.1	17.5
100 to 150	....	1.4	15.3
150 to 200	....	....	10.8
Minus 200	....	0.9	42.6

CHARACTERISTICS OF UNFIRED NOVACULITE BRIQUETS

EFFECT OF AMOUNT OF TEMPERING WATER ON THE MODULUS OF RUPTURE

Grain-size gradings.—The two grain-size gradings used were designated as "A" and "B." The "A" grading was that naturally obtained when 120 pounds of rock was ground 15 minutes in a wet pan. The "B" grading was the distribution computed from the equation:[9]

$$d = P^2 D \times 10^{-4}$$

Testing procedure. — Each batch was large enough to form 10 specimens, and after adding 2 percent CaO as limewater, it was mixed as thoroughly as possible by hand, then tamped into a 1 by 1 by 7 inch mold. The tamping force may be described as medium. After drying, the samples were tested for transverse strength. The data are shown in figure 26. These curves show maximum strength to be at a certain optimum water content. Both the maximum strength and the optimum water content varied with the grain-size grading. The maximum strength and optimum water content will also be found to depend upon the ramming pressure.

EFFECT OF PARTICLE GRADING ON THE MODULUS OF RUPTURE

Testing procedure.—It was noted in previous experiments that the optimum water content could be judged fairly well from the "feel" of the wet mixture. This procedure was used in the preparation of the samples for the tests described in this section. The batches were prepared with 3 percent CaO (added as lime water), and the amount of water most appropriate for the mix. Briquets were formed by ramming the wet batch into a 1 by 1 by 7 inch steel mold.

Two ramming pressures were used for this series of tests. In the lower pressure ram, the mix was tamped into the mold by ramming with the end of a 10-inch spatula handle which was held vertically in the hand and brought down into the mix with as much force as possible. The higher ramming pressure was obtained by fitting a wooden plug into the mold and driving it with a wooden mallet. This procedure could be used to fill the mold about two-thirds full. To complete the job, a large excess of batch was piled on top of the mold and then beaten down into the mold by heavy blows from the mallet.

Grain sizes.—The particle gradings are shown in figure 25. Mixtures were chosen so as to cross the minimum void area in this figure.

Results of modulus of rupture tests.—The compositions are shown in figure 25 and the results of these tests are summarized in table 14 and figure 25. The specimens formed by the high ramming pressure gave fairly uniform results, while the low ramming pressure produced specimens with

[9] Taylor and Thompson. Concrete—Plane and Reinforced, p. 775.
D = diameter of largest grain.
d = any chosen diameter.
P = per cent of mixture smaller than any given diameter.

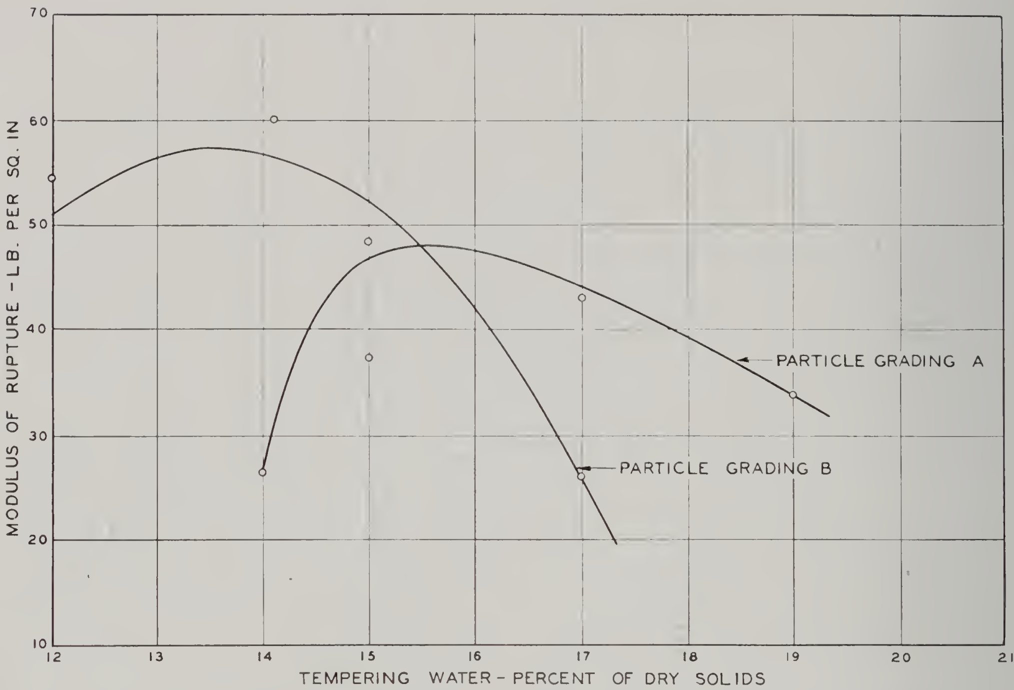

FIG. 26.—Effect of amount of tempering water used on the modulus of rupture of unfired novaculite briquets, CaO constant.

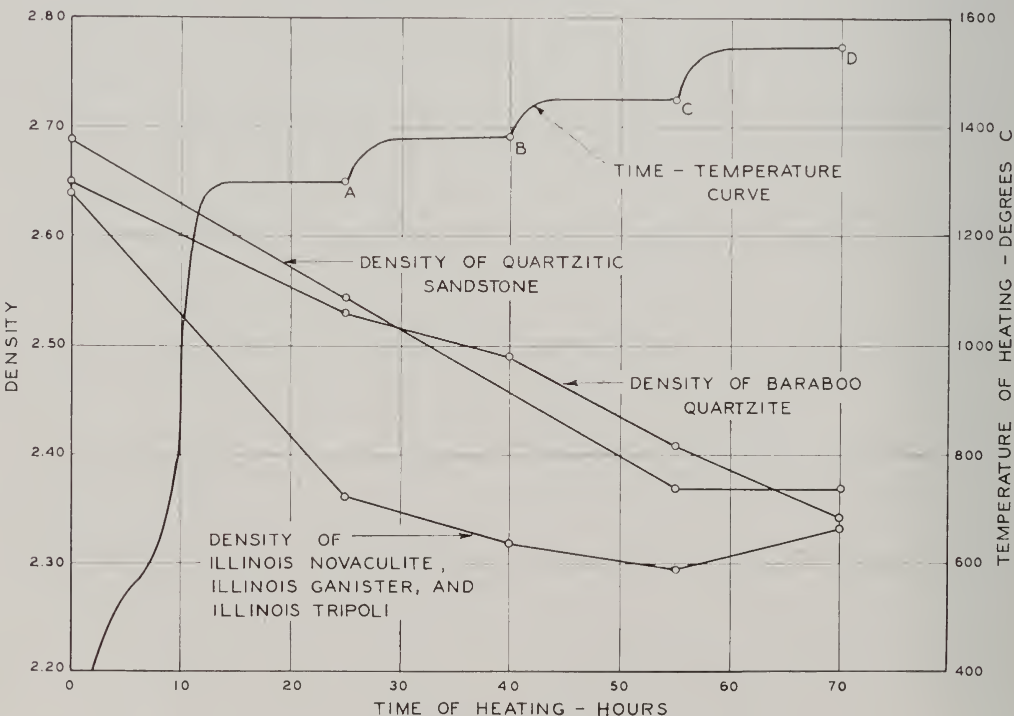

FIG. 27.—Firing schedule and rates of inversion.

wide variation in strength. Specimens formed by high ramming pressure varied from the mean by a maximum of but 6.8 percent, but those made by the low ramming pressure showed a 43 percent variation. In general the low ramming pressure produced bars having 30 to 80 percent of the strength of the high ramming pressure specimens.

Reference to figure 25 shows that the maximum strength was possessed by those specimens whose grain sizes fell within the densest packing area. The grain-size distribution is indicated by the coordinates on the graph, and the transverse strengths of the briquets are indicated by the arrows. The strengths are shown in a little more detail in table 14. These data show that the strength is a function of the density of packing of the grains in the brick. As the forming pressure increases, the porosity decreases and the strength increases. This change with pressure becomes very small at higher pressures. The most uniform results are obtained in this upper range of pressures.

Table 13.—Grain-size Distribution of the Minimum Void Mixture Determined by Packing Experiments

Sieve mesh	Wt. percent
	6.6
6 to 8	14.3
8 to 10	11.8
10 to 20	9.1
20 to 28	5.7
28 to 48	8.8
48 to 100	9.1
100 to 150	7.8
150 to 200	5.4
Minus 200	21.4

Rate of Inversion

NOVACULITE AND OTHER SILICA MATERIALS

Method of study.—The materials chosen for study were Illinois tripoli, novaculite, Baraboo quartzite, Illinois ganister, and an Illinois quartzite-sandstone. The same grain-size distribution was used in all the specimens, that is, the optimum grain-size found by the packing experiments, and shown in table 13. Each material was mixed with freshly slaked milk of lime, so that the CaO content of each specimen was 2.0 percent. The specimens were formed by ramming tightly in a 1 by 1 by 4 inch mold.

The molded pieces were put in refractory trays as an aid in making draw trials from a hot furnace. Each tray contained one specimen of each type of silica. These were fired in a gas kiln according to the heating schedule shown in figure 27. Samples were drawn from the furnace after treatments as indicated at A, B, C, and D. As soon as drawn, they were thrown into a crucible partially filled with sand and placed in a furnace heated at a temperature of about 800° C. After covering the samples with hot sand they were allowed to cool slowly to room temperature. The cold samples were pulverized to pass 200 mesh, and the density of the powders wetted *in vacuo* was determined in pycnometers.

Results.—The results are shown in figure 27. The Baraboo quartzite showed a steady decrease in specific gravity, and after the entire heat treatment the average density of the material was 2.345, indicating the presence of some uninverted quartz. There was some tridymite present, but the predominating portion was cristobalite.

Table 14.—Modulus of Rupture of Unfired Silica Brick
In pounds per square inch

	No. 5 Ramming pressure		No. 8 Ramming pressure		No. 10 Ramming pressure		No. 12 Ramming pressure		No. R Ramming pressure
	High	Low	High	Low	High	Low	High	Low	Med.
High	192	110	193	148	184	109	163	129	80
Low	169	64	181	62	169	46	151	70	50
Average	180	87	189	107	179	81	157	90	70

Microscopic examinations revealed the quartz to be the cores of large grains.

The curve for the Illinois quartzite-sandstone was very similar to that of Baraboo quartzite. The quartzitic sandstone was high in fluxing materials, which increased the specific gravity somewhat. There was very little uninverted quartz in the sample after the full heat treatment, yet its density was 2.37, due to the presence of heavier impurities.

The curves for Illinois ganister, tripoli and novaculite are identical and show a much greater rate of inversion than the other silica samples. The minimum density shown at the C draw contained considerable tridymite, as the higher temperature (above 1470° C.) showed an increase from 2.30 to 2.33 in average density. Aside from impurities and the bonding agent, the Illinois ganister and the novaculite after the D treatment were pure cristobalite, and no quartz was present. An appreciable amount of tridymite had been formed by the B treatment. The effect of the B and C treatment was to increase the tridymite.

Experiments with Standard 9-inch Shapes

General method.—Standard 9-inch brick were made in the laboratory by hand molding and were fired in a regular commercial kiln. The following properties were examined:

a. Modulus of rupture.
b. Deformation under load at high temperatures.
c. True density.
d. Porosity.
e. Exterior volume changes.
f. Over-all changes in length.
g. Microstructure.
h. Thermal expansion.

Details of procedure.—Raw materials included:

a. Selected white novaculite (clean).
b. Novaculite gravel and associated red clay.
c. Washed novaculite gravel.
d. Quartzitic sandstone.

All these materials contained the iron from the crushing operations.

Preparation of Bonding Agents

lime bonds

High quality lime was slaked in an excess of distilled water, screened through a 120-mesh sieve, and put in a 10-liter glass carboy. The CaO content per cc of suspension was determined by analysis.

special bond

A special bond was prepared by fusing the following mixture: 130 parts $BaCO_3$, 177 parts H_3BO_3, and 100 parts Fe_2O_3. This fusion, designated as FB-10, was pulverized to pass a 200-mesh screen and mixed with sufficient lime water to form two parts CaO to one part of the fused mixture.

Preparation of Specimens

grinding and mixing

The mine-run novaculite gravel was put directly into a wet pan together with the lime water and was ground for 15 minutes. The screen analysis of this mix is shown in table 15.

The selected novaculite rock was reduced in a jaw crusher, then put in a wet pan with the required amount of bond and ground for 15 minutes. The same treatment was given the quartzitic sandstone.

The washed novaculite gravel was ground dry in a wet pan and divided into three fractions as described on page 13. The bond and water were added to these batches, then mixed carefully by hand. The grain sizes of the different mixes are indicated under the proper heading in table 15.

Table 15.—Kind of Raw Material, Grain Sizes, and Particle Grading of Experimental Brick

Screen mesh	Novaculite, selected	Novaculite, mine-run gravel	Quartzite sandstone	Novaculite gravel, washed		
	Brick No.					
	CP-2, CP-3, CP-7	CM-0, CM-2	Q S	WN-I WN-II	WN-III	485
	Percentage on screen					
Plus 6	13.3	....	20.1	6.6	None	None
6 to 8	....	12.0	6.7	14.3	17.3	None
8 to 10	17.4	6.8	4.7	11.8	14.5	None
10 to 20	....	....	....	9.1	9.1	18.0
20 to 28	23.0	24.2	7.4	5.7	5.7	15.9
28 to 48	13.0	15.8	3.9	8.8	8.8	20.2
48 to 100	11.6	17.2	30.9	9.1	9.1	8.8
100 to 150	....	....	....	7.8	7.8	8.6
150 to 200	11.2	14.4	3.9	5.4	5.4	4.8
Minus 200	9.6	10.0	22.3	21.4	21.4	
Minus 200 to 325	....	....	....	....	....	8.7
Minus 325	....	....	....	....	....	15.0

Making the Brick

The wet batches were pounded firmly into a mold and the bricks thus formed were removed and allowed to dry a few days in air before going to the dryer. The kind of material used, the kind and amount of bond, and the designation numbers of the brick are shown in table 16.

The gradings of the CP series and the CM series are the natural gradings obtained from the respective materials when ground in the laboratory wet pan. The same is true of the quartzitic sandstone brick. The grading used in the WN-I and the WN-II brick was that which was shown in previous tests to be the optimum grain-size distribution. The size distribution of batch No. WN-III was the same as WN-I and WN-II except that the coarsest grains were through 6-mesh on 8-mesh. Number 485 had a maximum grain diameter of through 10-mesh on 20-mesh. This requires the addition of 15 percent of silica finer than 325-mesh. For this fraction, minus 325-mesh tripoli was used.

The brick were fired with commercial silica brick in periodic kilns.

Properties of the Test Brick

modulus of rupture

In the cross-breaking test, silica brick always fail in tension by tearing apart below the neutral axis. For this reason the test can be considered as a satisfactory measure of the degree to which brick are bonded together. As the strength and durability of silica refractories are limited largely by the degree to which fragments are bonded, this is a rather important test.

The cross-breaking strength data of some novaculite experimental brick are shown in table 16. The kind of raw material, particle grading, and brick numbers will be found in table 15. Brick No. CM-2 was the weakest of all. Too much water was used in the batch and the result was a high porosity (33 percent), and a weak bond. The individual grains in this brick were somewhat shattered. This sugggests that good brick cannot be made from novaculite unless the grains are forced tightly together during the forming process. Brick No. 485 had the highest modulus of rupture of any brick tested, and also the lowest porosity. The other brick, being intermediate be-

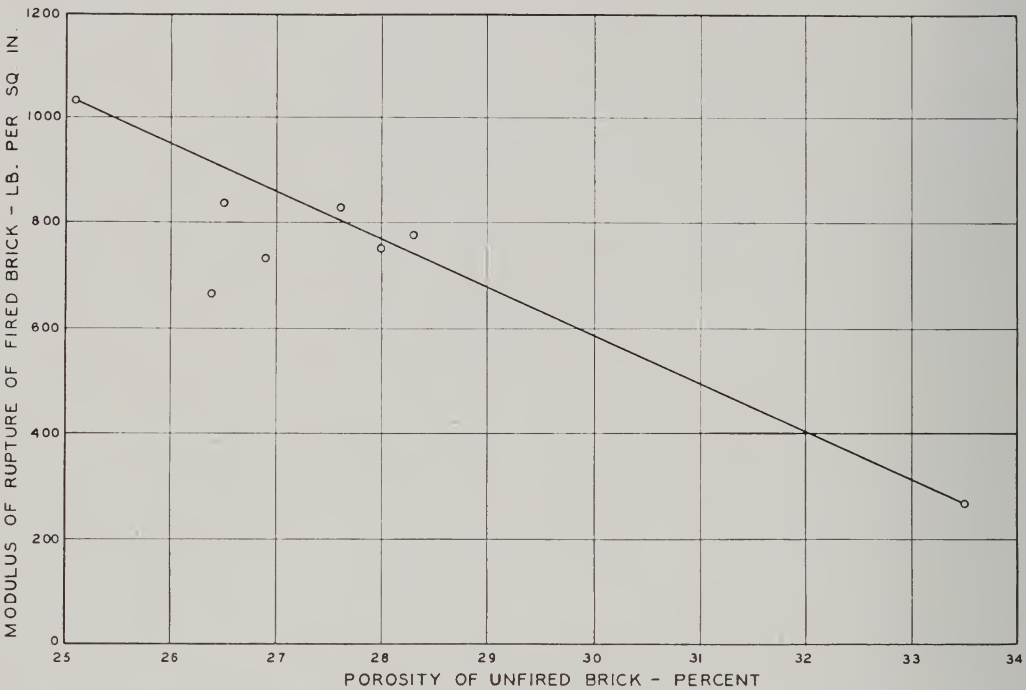

FIG. 28.—Porosity of unfired brick versus modulus of rupture of fired brick.

TABLE 16.—DATA ON 9-INCH NOVACULITE BRICK FIRED IN COMMERCIAL KILN

Material	Brick No.	Bond	Change during firing		Porosity		Density after firing	Modulus of rupture lb. per sq. in.
			Length %	Volume %	Unfired %	Fired %		
Novaculite crude gravel......	CM–O	None	4.1	13.2	25.6	....	...	339
Novaculite crude gravel......	CM–2	2.0% CaO	2.7	...	33.5	....	2.33	271
Massive novaculite..	CP–2	2.0% CaO	3.1	9.4	28.3	27.2	2.32	779
Massive novaculite..	CP–3	3.0% CaO	3.5	9.5	28.0	26.9	2.30	754
Massive novaculite..	CP–7	2.0% CaO + 1% FB 10	3.1	9.1	27.6	27.6	2.30	829
Quartzite sandstone.	QS	3% CaO	5.0	15.0	....	....	....	724
Washed novaculite gravel...........	WN–I	2% CaO	2.6	8.0	26.5	24.5	...	839
Washed novaculite gravel..........	WN–II	3% CaO	2.8	8.4	26.9	25.8	....	732
Washed novaculite gravel..........	WN–III	3% CaO	3.0	9.0	26.4	25.3	...	664
Washed novaculite gravel..........	485	3% CaO	1.6	4.9	25.1	24.8	2.29	1037
Commercial brick made from quartzite	...	...	...	...	...	...	...	791

tween these two extremes in porosity, are likewise intermediate in their modulus of rupture values.

There is a rough relationship between the modulus of rupture and the corresponding porosities (unfired) of all the 9-inch experimental bonded novaculite brick. The porosity of the unfired brick has been plotted against the modulus of rupture of the fired brick in figure 28. In these brick, the CaO varied between 2.0 and 3.0 percent. They were all given the same heat treatment during firing. These data show that the raw porosity, or factors which influence the porosity of unfired silica brick, will, under the influence of the same firing treatment, exert a predominating influence on the strength of the brick. The effect of the amount of CaO used as a bond may be observed by comparing CP-2 with CP-3 and WN-I with W-II. The only difference between CP-2 and CP-3 and between WN-I and WN-II, in the raw state, was the amount of CaO, as may be seen from tables 15 and 16. CP-2 with 2 percent CaO was stronger than CP-3 which had 3 percent CaO, and WN-I with 2 percent CaO was stronger than WN-II containing 3 percent CaO. It is evident from these data that increasing the lime from 2 to 3 percent decreased the strength under the given firing conditions. A similar comparison may be made between brick WN-II and brick WN-III. The only difference between these brick is that the maximum grain of brick was 8-mesh, whereas in brick WN-II it was 6-mesh. The lime content was 3 percent in each case. Under the same firing conditions, the effect of increasing the flux content was the same as reducing the maximum grain size. The rate of inversion of silica was hastened by increasing the flux content and also increased by decreasing the grain size. Too fast inversion of silica caused weakening of the structure of the brick. This suggests that brick such as CP-3, WN-II and WN-III, could be improved by a slower rate of temperature increase in the early part of the inversion period (about 1100° to 1150° C).

Brick No. 485 apparently does not follow these rules, since it is the finest grained mixture and is also composed of 3 percent CaO. No batch of this grain size grading was made using 2 percent CaO, so it cannot be said whether the higher strength in this case would result from the 2 percent or 3 percent lime bond. It probably would be decreased by decreasing the amount of bond, because the great decrease in the grain size had no adverse influence on the strength of the brick. In former experiments it was noted that rapid inversion caused pronounced swelling and cracking in specimens which contained coarse grains, but this did not happen when the specimens contained no coarse grains.

DEFORMATION UNDER LOAD AT HIGH TEMPERATURES

Bricks CP-2 and CP-3 were heated to 1500°C under a load of 25 pounds per square inch, according to the A.S.T.M. method. After this treatment the brick had increased in length 0.03 percent.

POROSITY CHANGES DURING FIRING

The porosity, both in the fired and unfired brick, was computed from the true densities and the exterior volumes of the specimens. In every case there was a decrease in porosity due to firing. The porosity was usually about one percent less after firing than before.

The difference in bulk volumes before and after firing was less than theoretical. The volume changes of the various specimens varied between 8 and 9 percent of the permanent exterior volume expansion from unfired to fired condition. The true-volume expansion was about 15 percent. This means that there was some sort of shrinkage taking place which counteracted part of the expansion due to inversion.

It is interesting to compare the volume changes shown in table 16 of brick WN-I, WN-II, and WN-III. No. WN-I with 2.0 percent CaO, had a bulk volume expansion of 8.0 percent and a transverse strength of 839 pounds per square inch. WN-11, differing from WN-I only in its CaO content, had an exterior expansion of 8.4 percent and a modulus of 732. WN-III, simi-

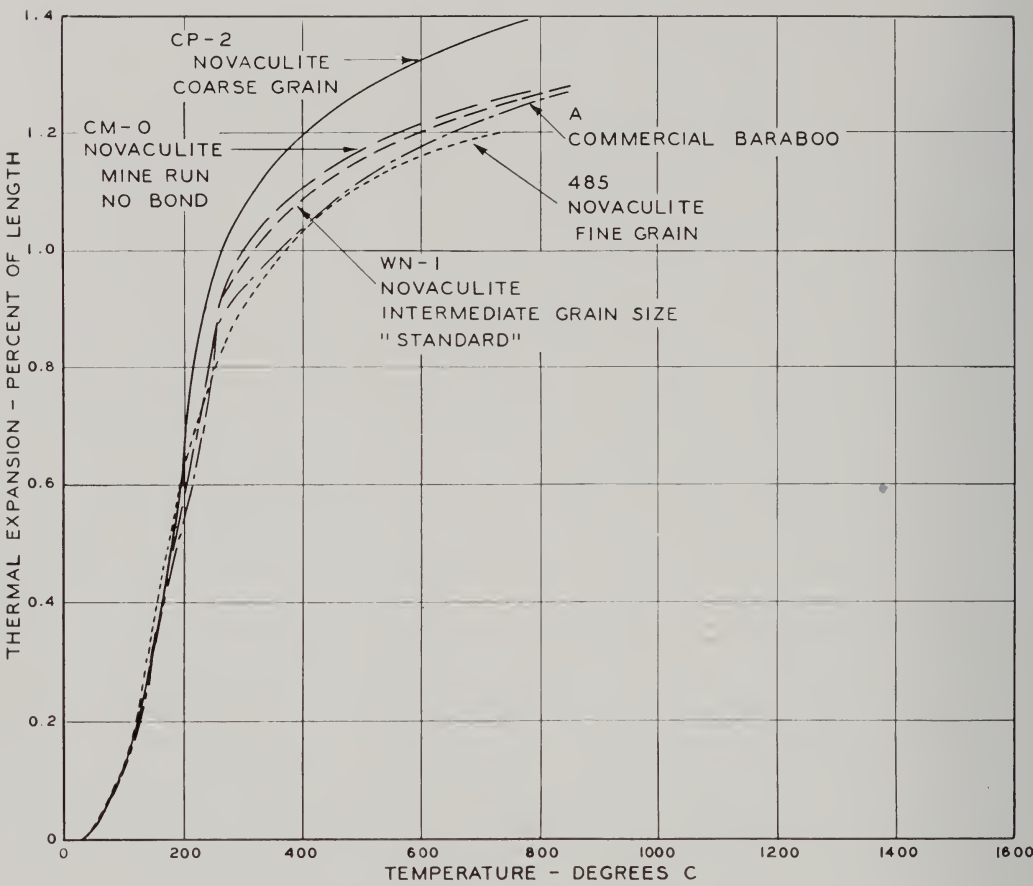

FIG. 29.—Thermal expansion, percent length versus temperature.

lar to WN-II but of smaller maximum grain size, had still higher volume expansion and lower strength. This is in accord with the conclusion that reduction in strength is caused by rapid inversion promoted by increasing the flux content or decreasing the grain size.

Brick 485 increased only 4.9 percent by volume during firing. This small volume increase remains unaccounted for, unless it be assumed to be characteristic of the material.

MICROSTRUCTURE

The coarse grains are composed of very small crystals of cristobalite. Only rarely was any quartz observed. Some quartz was found in the center of grains that were larger than $\frac{1}{4}$ inch in diameter. In cross-sections made from WN-I, WN-II, WN-III, and 485, no quartz was found. The coarse grains were all cristobalite, while in the groundmass, where the fine silica was in contact with lime, good tridymite development was noted. The tridymite crystals were developed much better in brick 485 than in any other, and much better in the WN brick than in the CP brick. Novaculite brick were consistently lower in quartz content than quartzite brick. The CP brick were rather coarse grained, with a high percentage of very coarse grains and a deficiency of fines. These brick were rather poor in tridymite and rich in cristobalite, and almost free of quartz.

A peculiarity noted in the microstructure of the novaculite brick was the presence of fine spherical specks in the larger grains which had inverted to cristobalite. These specks appeared to be small pores which presumably are related to the slightly porous nature of the raw novaculite.

THERMAL EXPANSION

The thermal expansion of some experimental novaculite brick and a commercial quartzite brick are shown in figure 29. Brick CP-2 was a coarse-grained brick composed almost entirely of cristobalite. CM-O was an unbonded brick made from crushed mine-run novaculite gravel. Brick WN-I has a thermal expansion very similar to that of a typical commercial brick. No. 485 had a definitely lower thermal expansion than the commercial quartzite brick used for comparison. Under the same firing treatment, the thermal expansion decreases with decreasing grain size.

Conclusions

The compact massive novaculite is of sufficient purity to make a high grade silica brick, and may be crushed to yield desirable distribution of grain sizes. The novaculite gravel may easily be washed to remove the associated clay, after which it has properties similar to the massive pure rock.

The strength of fired silica brick depend largely upon the manner in which the brick is made. The grain-size distribution of the siliceous material determines the density to which the mass can be packed, has an important influence upon the strength of the resulting fired brick, and influences the thermal expansion by fixing the ratio of cristobalite to tridymite. The transverse strengths of fired silica brick are roughly proportional to their corresponding porosites in the unfired state. Too rapid inversion of novaculite causes a weakening of the brick. This may be influenced by the grain size, the amount of bond, or the manner of firing. Novaculite with the same particle grading and same CaO content as commercial quartzite brick yield about the same type of brick as the commercial quartzite. Novaculite should be fired a little more slowly than the quartzite in the early stages of the inversion. High quality brick were obtained when novaculite was fired according to standard commercial silica brick practice.

Novaculite brick have a smaller exterior overall expansion than quartzite brick. When made with a maximum grain size of 6-mesh and with 2 percent CaO, the over-all expansion was 8.0 by volume. With a maximum grain size of 10-mesh and 3 percent CaO the over-all expansion was 4.9 percent by volume. This small expansion has been ascribed to a shrinkage of the novaculite itself.

Better brick were made when fine grained material was used. The extremely fine fraction may be added as Illinois tripoli. For best results with novaculite, it is recommended that a mix similar to the one designated as No. 485 be used.

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